2009

Enzyme modified soy flour adhesives

John F. Schmitz
Iowa State University

Enzyme modified soy flour adhesives

by

John F. Schmitz, Jr.

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-majors: Food Science and Human Nutrition; Biorenewable Resources and Technology

Program of Study Committee:
Deland Myers, Co-Major Professor
Lawrence Johnson, Co-Major Professor
Petrutza Caragea
Michael Kessler
Monlin Kuo
Tong Wang

Iowa State University

Ames, Iowa

2009

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AMSP - alkaline modified soy protein isolate

ANOVA - analysis of variance

ANSI - American National Standards Institute

ASTM - American Society for Testing and Methods

BWT - boiling water test

cps - centipoise

DH - degree of hydrolysis

DOPA - 3,4-dihydroxyphenyl-alanine

GH - guanidine hydrochloride

GLM - general linear model (SAS statistical analysis model)

HS90 - HoneySoy90 (defatted soybean flour from Cenex Harvest States)

IB - internal bond strength

MDF - medium density fiberboard

MDI - methylene diphenyl diisocyanate

MMT - million metric tons

MOE - modulus of elasticity

MOR - modulus of rupture

OPA - o-phthaldialdehyde (reagent used in degree of hydrolysis measurement)

PAE - polyamide-epichlorohydrin

pI - isoelectric point

PF - phenol formaldehyde (petroleum based synthetic resin)

PRF - phenol resorcinol formaldehyde

SDBS - sodium dodecyl benzene sulfonate

SDS - sodium dodecyl sulfate

SPC - soy protein concentrate

SF - soy flour

SPI - soy protein isolate

TMSP - trypsin modified soy protein

TS-2B - thickness swell after 2-h boiling test

TS-24S - thickness swell after 24-h soaking test

UF - urea formaldehyde

WSAD - water soaking and drying test

ABSTRACT

Soy protein based adhesives have not been used extensively in wood products since the 1960's because of inferior performance, stability, and water resistance issues relative to petroleum based adhesives. The early soy protein adhesives were made from defatted flours and were dispersed in alkaline solutions to denature proteins and make more polar groups available for adhesion. Recent research has focused on soy flour (SF) and soy protein isolate (SPI) adhesives due to increased phenol prices and concerns over the use and exposure to formaldehyde. In the present work enzyme hydrolysates of SF and SPI were evaluated in phenol formaldehyde (PF) and polyamide-epichlorohydrin (PAE) adhesive formulations. In soy/PF blends the degree of hydrolysis (DH) was an integral factor in both strength and durability. DH >18% was detrimental to the internal bond and thickness swell of medium density fiberboard (MDF) specimens with PF blends. MDF made with blends of hydrolyzed SF/PF with up to 20% soy solids did not significantly differ in strength or durability compared to pure PF resin. Addition of hydrolyzed SF to the adhesive matrix increased the modulus of elasticity of MDF.

Similar results were observed when hydrolyzed soy flour was incorporated with PAE. Hydrolysis of SF led to lower viscosity resins, but DH >10% decreased shear strength of plywood specimens. PAE is known commercially for its wet strength attributes, but when PAE was <10% of the resin formulation, lap shear samples delaminated during wet strength testing. In both plywood and MDF

systems, the addition of urea to soy flour hydrolysates before combining with PAE increased the wet strength and dimensional stability of finished products.

CHAPTER 1

General Introduction

Thesis Organization

This dissertation includes four research chapters. Chapters 2-5 are manuscripts that will be submitted for publication in *Industrial Crops and Products* and *Journal of the American Oil Chemists Society*. Within the four chapters two unique resin systems were evaluated. In chapter 2 phenol formaldehyde (PF) was blended with enzyme modified soy protein isolate and soy flour (SF). Medium density fiberboard (MDF) was used as a model system and means for testing different soy/PF resin blends. Chapter 3 also examines PF, but only with SF blended into the resin. The main focus of this research was to characterize the effects of protein hydrolysis on MDF product quality. The final two research studies included in the dissertation continue to evaluate enzyme modified SF as an adhesive, but from a different angle. In chapters 4 and 5, SF is the predominant ingredient in the adhesive formulation and is crosslinked with polyamide-epichlorohydrin (PAE), a sizing agent used in the paper industry to increase wet strength. Each of these studies provides insight into the use of SF hydrolysates as an ingredient in formaldehyde free wood adhesive formulations. A final summary is discussed in Chapter 6 along with brief remarks on the current state of soy based adhesives.

Literature Review

There are growing consumer and political interests in achieving high contents of biobased materials in consumer goods to meet increasing expectations for sustainability and use of renewable resources. Along with these consumer and legislative trends, more stringent environmental standards, increased ability to deliver improved performance properties, and more cost-effective chemical conversion processes are driving increased usage of soybean products as feedstocks and materials for industrial products. From 1999-2007, worldwide production of soybean meal increased from approximately 108 to 150 million metric tons (MMT). Ending stocks for meal have risen to as high as 6.8 MMT from ending stocks of 4.1 MMT in 1999 (1).

These factors provide incentive to develop new materials from soybeans, which can create new markets for this important crop. Additional initiatives to promote developing biobased products to replace petroleum derived products have been implemented by the United States Congress through enacting the Biomass Research and Development Act of 2000 and Executive Order 13134, “Developing and Promoting Bio-based Products and Bio-Energy,” which set a national goal of “tripling the use of biobased products and bioenergy by 2010.” This is projected to create $15-20 billion in new income for farmers and reduce fossil fuel emissions by up to 100 MMT of carbon.

Early Soybean Uses in Industrial Biobased Products

There are no current industrial uses for whole soybeans in biobased

products, but there are historical accounts of soybeans being used as ship ballast (2) and powdered soybeans were patented as a flooring cover. The first industrial uses of soybeans in the United States helped the country emerge from the Great Depression by providing various consumer goods as a result of the Chemurgy Movement. In current markets, the most prominent industrial soybean use is soybean oil for manufacturing biodiesel, but the uses of soybean oil and meal are also growing in other markets.

Soybeans were first domesticated in northeastern China around the 11th century B.C. The Chinese were the first to crush soybeans into oil and cake by using mechanical presses. Oil was primarily used for cooking, but records indicate it was also used for lubricating fluids, lamp oils, coatings, and marine caulking materials (9). The oldest known industrial use of soybeans dates from 980 A.D., when soybean oil was first used in caulking compounds for boats (4). Up until the 20th Century, the Chinese used the deoiled cake for another important industrial purpose, soil amendments and fertilizer, often referred to in the early literature as green manure or bean cake manure (5, 6). Reportedly, soybeans were first introduced into North America in 1804 as the ballast of a Yankee sailing ship involved in trade with China (2); thus, ship ballast became the first industrial use for soybeans in the West. It was not until the late 19th Century, however, that soybeans began to attract the serious attention of Western scientists, farmers, and businesses. The first commercial uses for soybeans in the United States were industrial, because soybean oil was regarded as inferior to alternative food oils due to flavor instability. In 1910 flax, the primary industrial oil crop at that time,

escalated in price, and soybean oil began to be used either as a substitute or extender for linseed oil, which was widely used in paints and varnishes.

Soy Protein

Soy Protein Products and Characterization. Soybean plants are legumes that originated in eastern Asia (7). Soybeans are typically processed by cracking the seed, dehulling, drying, flaking, extracting oil, redrying, and milling the coproducts into useful fractions (8). Coproducts of the milling process include soy flours, from which soy protein concentrates and isolates can by produced, which are all defined by protein content (9). Defatted soy flours are the least refined coproduct and are produced by simply grinding defatted soybeans. They are commonly comprised of 44-50% protein, 30% carbohydrates, and 20-25% fiber, ash, and water (10). Soy protein concentrates are comprised of 65-72% protein, 20-22% carbohydrates, and 7.5-10% fiber and ash. Soy protein isolates are the most refined coproduct and represent the highest overall protein concentration. Soy protein isolates contain at least 90% protein on a dry basis (11). Soy protein products vary not only in protein concentration, but depending on the processing conditions, can vary based on particle size, solubility, water absorption, color, nutritional quality, viscosity, and adhesive quality (9).

Although carbohydrates play roles in water binding and viscosity, proteins are the primary functional component in soy coproducts (12). In general terms, protein is a polymer of α-amino carboxylic acids linked by peptide bonds. All proteins contain a peptide backbone, but the distinguishing characteristics of

proteins are the sequence of side groups disseminating from the peptide backbone. Soybeans commonly have eighteen different amino acids with different functional side groups. These side groups include hydrocarbons, amines, carboxylic acid, hydroxyl, thiols, and phenolic groups (13). Side groups on the peptide chain represent the majority of reactive sites of proteins, and each side group undergoes various reactions, reacting with other amino acids or other reactants.

Proteins have primary, secondary, tertiary, and quaternary structures. Primary structure is the amino acid sequence linked by peptide bonds (11). Secondary structure is the relative position of amino acids within a polypeptide chain, which determines the formation of helices and sheets. Tertiary protein structure is related to the position of a portion of the peptide chain with respect to other parts of the same peptide chain, and quaternary structure is the arrangement in space of one peptide chain with other peptide chains (14). Proteins fit into two broad macromolecular classes. The first is fibrous proteins which are insoluble in water. The second are globular proteins. Globular proteins are soluble in aqueous solutions of acids or bases (13). Globular protein structure is stabilized by intermolecular forces including van der Waals' forces, hydrophobic interactions, ionic bonds, hydrogen bonds, and disulfide bonds. Soy proteins are globular proteins with numerous polypeptide chains folded into compact, interconnected units. Protein structure not only determines solubility, but also affects other functional properties (12).

As mentioned previously, the carbohydrate fraction in soy flours is approximately 30%, whereas protein isolates have only about 1% carbohydrate (15).

Carbohydrate moieties in protein isolates are held in place either by covalent bonds to the polypeptide chain or van der Waals' forces (11). Carbohydrate fractions have various levels of impact in soy coproducts related to the amount of carbohydrate present and the specific use. Residual lipids, fiber, and ash also exist in varying amounts, however, they have limited effects on physical and functional properties (12).

Soy Protein Properties. Water solubility is considered one of the primary physical characteristics of soy proteins (16). The major soy proteins are globulins, which are insoluble at their isoelectric point (pI). They are, however, soluble in water or salt solutions above or below their pI (17). Soy proteins have limited solubility between pH 3.75 and 5.25. The maximum solubility was observed at pH 1.5-2.5 and pH >6.3 (19). Insolubility of protein between pH 3.75 and 5.25 is a result of soy proteins pI of 4.5. A range of solubilities can be obtained for soybean proteins by using different heat or chemical treatments. Likewise, soy proteins can be made soluble near the pI by hydrolysis of the native protein state into smaller peptide chains (18). Hydrolysis of the native state alters the charge distribution of the protein creating peptides that are insoluble at different pH (19).

Protein interactions with water are important to viscosity and general dispersibility. The viscosity of protein dispersions is influenced primarily by intrinsic factors. Likewise, intrinsic factors can be altered by environmental factors such as pH and exposure to heat, which in turn alter the intrinsic structure and interactions

in proteins (18). Along with other factors, these two properties directly influence the utilization of soy proteins in industrial applications.

Soy Protein Modifications

Soy proteins are used in a variety of food and non-food applications. Soybean proteins have many functional properties that have been demonstrated in a variety of food applications (17,18). Functional properties are any physico-chemical properties that change the processing or behavior, and quality of protein in food or non-food applications (18). The required functional properties for soy proteins change with the type of application, but the large variety of side groups present in soybeans leads to many diverse functional capabilities. Research efforts continue to look at novel industrial application of soybean proteins.

In wood adhesive applications, the desired functional properties include adhesion, water solubility, water resistance, and viscosity. Unmodified soy proteins cannot meet all functional properties needed for adhesive applications (19). Functional properties can be improved by modification of protein structure or properties such as disulfide bonds, molecular size, and net charge (18). Soy proteins can be made to have varied functional properties through physical, chemical, or enzymatic modifications (20).

Denaturation. Soy proteins are compact molecules, folded in on themselves at numerous locations (18). Denaturation refers to any modifications which change the native quaternary, tertiary, or secondary structure, but do not alter the primary

amino acid sequence. Denaturation is also commonly known as protein unfolding and occurs by breaking hydrogen and disulfide bonds within higher orders of protein structure (21). Denaturation therefore leads to increased availability of amino acid side groups that were previously hidden within the internal structure of proteins (22).

Alkaline solutions have been used extensively to denature soy proteins. The early soy adhesives were alkaline dispersions and more recent work has shown such treatments improve solubility, adhesive properties, and decrease viscosity (8, 19, 23, 24). Sun *et al.* (25) showed alkaline dispersions increase protein unfolding of soy protein, resulting in increased exposure of internal hydrophobic groups. Strong alkaline dispersions are necessary to increase solubility and adhesive properties, but high concentrations of alkali also causes staining of wood surfaces that is unacceptable for products with visible surfaces (19, 26).

Urea can also be used to denature protein. Urea interacts with hydroxyl side chains and decreases hydrogen bonding within the protein structure (27). Wolf (17) reported on the dissociation and unfolding of soybean proteins in the presence of urea, and Nir *et al.* (26) showed the viscosities of soy protein dispersions decreased with increasing urea concentrations. In addition to lower viscosity, urea-modified soy proteins were shown to have higher shear strength and water resistance than unmodified soy proteins in wood adhesive applications (25).

Heating soy protein dispersions above 60°C leads to dissociation of subunits and unfolding of protein structure (20). When proteins are heated hydrophobic interactions breakdown and subunits dissociate. The increase in availability of

hydrophobic groups increases surface reactivity and improves the adhesive strength of protein materials (28). Heat denaturation, however, can lead to decreased solubility as well. Excessive denaturation due to heat will expose too many hydrophobic groups and decrease solubility due to the aggregation of hydrophobic groups (29).

Sulfites and thiols have also been used extensively to cleave disulfide bonds in proteins (12, 30). Unmodified soy proteins and those modified with sodium sulfite were compared by Kalapathy *et al*. (31). Sulfite modified proteins had decreased viscosity and increased adhesive strength due to less protein molecular interaction. The use of sodium hydroxide and sodium sulfite were therefore used to control viscosity and adhesive strength of modified proteins in adhesive applications.

Hydrolysis. Hydrolysis breaks the peptide bonds of the peptide backbone, causing cleavage of both primary and secondary structure. Hydrolysis of proteins leads to increased amine and carboxylic functional groups (22). Protein hydrolysis decreases peptide chain length and reduces both viscosity and molecular size (31). Short peptide chains have more functional groups exposed, which is believed to enhance the reaction of soy protein with chemical crosslinkers in adhesive formulations. If hydrolysis products are too small however functional properties can be lost (32).

Acid hydrolysis is used for quantitatively breaking protein into constituent amino acids. The specificity of acid hydrolysis and extent of hydrolysis are functions of the acid applied, temperature, pressure, acid concentration, and

presence of non-protein materials. Hydrochloric, sulfuric, and nitric acids have all been used as acid hydrolysis agents that result in very small peptide chains (33). Acid hydrolysis is not random, but instead has varying specificity that can be used to form peptides with specific end groups. Hydrolysis with some acids completely decomposes the amino acid tryptophan completely and converts glutamine and asparagine into glutamic acid and aspartic acid, respectively (34). Complete degradation of some amino acids, reversion of others, and an excessive level of hydrolysis in some cases makes acid hydrolysis an unsuitable technique to prepare soy protein for use in adhesive formulations (32).

Alkaline solutions can be used to both denature and hydrolyze soy protein. Hydrolysis of proteins occurs in solutions with >5% alkaline (35). Alkaline hydrolysis is a completely random process with no control over variation or quality from batch to batch. In addition, the strong alkaline condition causes the breakdown of amino acids and creation of others. As one example, serine can be decomposed under strong alkaline conditions to form glycine or alanine (34).

A third method of protein hydrolysis is through the use of protease enzymes to improve functional properties (18, 35.6, 37). Two types of hydrolysis have been tested: limited proteolysis and complete enzymatic hydrolysis. Enzymatic soy hydrolysates have improved solubilities and emulsification properties as well as decreased viscosities. The primary advantage of enzymatic hydrolysis is its high specificity and yield of peptide fractions. Small amounts of enzymes are required and processing conditions are safer than those for either acid or alkaline hydrolysis. Kim *et al.* (37) hydrolyzed soy protein isolates with trypsin, rennet, chymotrypsin,

and alcalase to obtain information on the effects of enzyme proteolysis on molecular and functional properties. Trypsin most effectively decreased the molecular size while retaining functional properties (38, 39).

Soy Protein as a Wood Adhesive

Alkaline Dispersions. Plywood adhesive was one of the major industrial uses for soybean products prior to World War II. The patents of 0. Johnson (40) and I. Laucks and G. Davidson (41) formed the basis for using soybean meal and protein in adhesives for the plywood industry in the late 1920's. Soy protein adhesives remained competitive in plywood applications after World War II and into the 1960's. The first soy adhesives were used in cold-press, clamping applications (19, 40). The cited advantages of soy glues were soy flour's low cost and plentiful supply compared with casein; its relatively strong and water resistant (albeit not waterproof) bond; its lack of tackiness, making the glue-coated surfaces and materials easier to handle and improving manufacturing efficiencies; its ability to be spread or sprayed in either hot or cold applications; and its compatibility with high moisture containing veneer without surface splitting (42).

Soy based Adhesive Performance Properties. Numerous adhesive models have been developed over the years. Most of the adhesion strength comes from three primary mechanisms however: a) chemical bonding, b) physical adsorption, and c) mechanical bonding (43). Improved protein functionality and performance are two reasons for modifying soy protein ingredients used in adhesive applications.

Functional modifications for use in adhesives are achieved by altering molecular conformations through physical, chemical or enzymatic agents at the secondary, tertiary and quaternary levels (44). Denaturing and cleaving disulfide bonds enhance adhesion and water resistance by unfolding the proteins and increasing their interaction with the wood (45). Protein or flour modification is also utilized to increase water resistance (46). The viscosity of soy protein dispersions can be varied by using salts or reducing agents without negatively affecting bond strength (39).

The strongest glue joints are formed when the chemical bonding is between the adherand and the adhesive. In wood products, adhesives must be highly polar to bond to cellulose wood fibers. To enhance strength and water resistance properties, it is also beneficial for adhesive systems to form high molecular weight, crosslinked networks. The adhesive performance of soybean proteins is dependent upon particle size, nature of the bonding surface, protein structure, viscosity, and pH (19). Other factors, which can also affect adhesive performance, are processing parameters such as press temperature, pressure, and time (19). The particle size of soybean meal or SPI used in adhesives significantly effects its suitability and performance. The smaller the particle size, the easier and more complete soy protein ingredients can be dispersed and modified with chemicals or enzymes.

Factors important to making soy protein ingredients good adhesive components are not completely understood, in part, because of the diversity of product applications and wide variety of adhesive functional needs. Protein is believed to be the primary wood bonding component, although when soy flour is

used, the roughly 35% carbohydrate content may also provide some additional surface adhesion properties. In theory, one would expect that a higher protein content ingredient than soy flour (44 to 52% protein), such as SPCor SPI, would give much greater bonding.

Adhesive properties are also dependent upon the nature of the surface to be bonded. If the bonding surface is too rough, cohesive failure results; surfaces that are too smooth cause adhesive failure. Rough surfaces produce random micro finger joint structures under pressure whereas smooth surfaces may produce less micro random finger joint effects, which may be responsible for the low bond strength. The major components in wood varies little from species to species, so variation in bond strength with the type of wood may be due to variation in physical properties such as surface roughness, grain and porosity.

The bond strength of a protein glue depends on its ability to disperse in water and on the interaction of non-polar and polar groups of the protein with wood. In native protein, the majority of functional groups are unavailable for bonding and adhesion due to protein folding caused by van der Waals forces, hydrogen bonds and hydrophobic interactions. As a result unmodified soy flour is highly viscous and a poor adhesive material. Modifications change internal bonds and uncoil the protein molecules. Denatured proteins can be enhanced further by hydrolyzing the protein into smaller peptides (19).

Viscosity is an important property, which largely governs adhesive behavior and performance (19). The operating viscosity limits of wood adhesives are very diverse ranging from 500 to 75,000 cps depending on the application. A working

viscosity of 500 to 5000 cps is commonly needed for gluing materials that are highly absorbent like soft board, dried wood aggregates or atomized/spray adhesive systems; 5,000 to 25,000 cps for either cold- or hot-press wood laminating applications; and >50,000 cps for wood laminating procedures. A viscosity range of 8,000 to 20,000 cps has been specified for no-clamp, cold-press adhesive applications (47). Unmodified soybean adhesive viscosities are dependant on the solids content, but less water is preferable to shorten drying/curing times (19). In high-concentration adhesives, high viscosity results from intermolecular interactions due to unfolded protein molecules. Electrostatic interactions and disulfide bonds between peptide chains are the major viscosity-forming forces in soybean meal or SPI dispersions. Most wood adhesives fit in the low viscosity range, and therefore soy protein requires modification for use in adhesives.

The effects of wood product manufacturing conditions, such as press time, temperature and soy protein concentration, on gluing strength and water resistance of soybean protein adhesives in fiberboard applications were reported by Zhong and Sun (48). Shear strength increases with increasing press time as well as press pressure at 25°C (77°F). Shear strength increases were observed for increased temperature as well primarily because curing and drying rates increase with temperature. Temperature effects were more pronounced at higher temperature. Shear strength of soaked samples decreased by 12-25%. A maximum protein content of 12% was observed.

The major advantage of soy glue is that it can be cured either hot or cold. Hot-curing typically occurs at temperatures between 200 and 250°C, pressure of

1.21 MPa and fast curing times (90-180 s) to prepare plywood panels (46). Another advantage of soy glue is that it can be used to bond green lumber without kiln drying. Using dry wood, cold-curing of soybean glues is recommended at 1.03-1.21 MPa pressure for 15 min. During clamping, soybean glues form films having sufficient gel strengths via dehydration to tightly hold plywood sheets even after pressure release. Complete adhesive cure is obtained at room temperature over several days but machining can be done after 6 h.

Alkali modification. Alkaline hydrolysis is also an effective means of reducing viscosity. Alkali helps to: (a) unfold the protein structure thus exposing all functional sites for interaction with wood; and (b) enhance the hydrolysis reaction, which in turn, affects viscosity as well as adhesive efficiency (39). Higher pH increases the rate of hydrolysis and leads to better bond strength and water resistance, but decreases storage life. At higher pH, viscosity decreases with storage time, which adversely affects adhesive properties. Optimum treatment conditions for alkali-modified soy protein (AMSP) that resulted in the highest bond strengths were 9.0/70°C (pH/temperature), 10.0/50°C, 11.0/50°C and 12.0/40°C. Discoloration of wood products made with AMSP occurred with adhesives made at pH >11 because alkali salts react with wood resulting in a brown color. Similar discoloration was noted in early adhesives in strong alkaline conditions (19), and therefore limits the potential use of adhesives from harsh alkaline treatments. Mild alkaline treatments including calcium hydroxide, disodium phosphate, and ammonia hydroxide were

tested, but are not suitable for wood product applications due to poor bond strength (19).

Soy protein ingredients used in adhesives have typically been modified using high sodium hydroxide concentrations and pressure. AMSP adhesive is stronger and more water resistant compared with adhesives containing unmodified soy protein (39).

Enzymatic modification. Proteases, such as trypsin, pepsin, papain and alcalase, have also been examined as modifiers (39, 25, 49). The advantages of enzymatic modification include high reaction rates, mild conditions using low cost processing equipment, and most importantly, the possibility of capitalizing on hydrolytic specificity to produce enhanced performance properties. Proteases hydrolyze peptide bonds thereby modifying proteins but leaving carbohydrates untouched. Modification of SPI with papain affected hydrophobicity, solubility and emulsifying properties (35.6). Papain-modified SPI has significantly higher solubility and better emulsifying properties. Trypsin-modified SPI (TMSP) has lower viscosity than unmodified SPI enabling adhesives with greater solids contents to be formulated (49). TMSP and trypsin-modified soybean flour have much higher bond strengths with soft maple compared unmodified SPI. Initially, bond strength increases with increased heating time at 120°C, but strength decreases with treatments over 1 h (39). Urea formaldehyde (UF) can be partially substituted with TMSP adhesive. The highest shear strength is reached when 30% UF adhesive is replaced by trypsin-modified soy components.

Cellulases are also useful in preparing soy flour for adhesives. Depending on adhesive application requirements, protease treatment alone may not reduce the viscosity to a workable range in high-solids-content materials.

Chemical modification. Certain reagents, such as urea, guanidine hydrochloride (GH), sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS), denature protein and improve bond strength and water resistance (42, 50-52). Chemical modifications with urea, GH, SDS and SDBS at low concentrations (<3 M) all increase the adhesive functionality of SPI (25, 50, 51). Urea and GH concentrations significantly affect the extent of protein unfolding and adhesive properties, but SDS- and SDBS-modified SPI give better water resistance as well as improved bond strength (51). Wet and dry heating, grinding, freezing, pressure, irradiating and exposing to high frequency sound waves can also be used to denature proteins, but adhesive functionality is diminished when soy protein is subjected to these treatments (19).

The effects of ionic strength on the functional properties of soy proteins have been well documented (12, 53, 30). Ionic surroundings weaken electrostatic interaction between protein molecules. Soy protein adhesives have also been modified to reduce viscosity by using ionic solutions. Concentrations of 0.1 M sodium chloride, sodium sulfate, or sodium sulfite reduce viscosity of soy protein with no significant adverse effects on bond strength and water resistance. Viscosity was reduced from 30,000 to 6000 cps with 0.1 M NaCl and 1050 cps with 0.1 M Na_2SO_4. A similar Na_2SO_3 treatment results in modified SPI with 110 cps viscosity

and 28% decrease in disufide linkages. Treating with >0.1 M of any ionic solution decreases viscosity further, but bond strength is also diminished (54).

Chemical modification with dopamine has also been used as strength and water resistance aids for SPI adhesives (55). Dopamine is an amino acid with two adjacent phenolic hydroxyl groups, and is the primary component responsible for marine adhesive properties. This modification creates an SPI, which is similar to mussel proteins used for surface adhesion. Increased water resistance compared to other stand-alone SPI adhesives has been achieved. Bond strength depends on the phenolic functionality in the synthesized compounds (55).

Blended adhesives. Adhesives with enhanced performance properties can be obtained by blending soy protein adhesives with other protein or synthetic adhesives. Blends of soy flour with blood, casein, phenol formaldehyde (PF), and phenol-resorcinol formaldehyde (PRF) have been used to develop wood glues with unique properties (56). Blended adhesives for biodegradable plant containers have been obtained by blending SPI with varying amounts of poly-(vinyl alcohol) or poly-(vinyl acetate) (57, 58). Blends of soy protein and PRF resins are useful in finger-jointing green lumber with the Honeymoon System (59-62). Soy protein and PRF blends cure rapidly at room temperature and have excellent water resistance and reduced formaldehyde emissions. Soy protein is also much less expensive than PRF adhesives.

Soy flour dispersed in sodium bisulfite solution has been blended with PF in a soy/PF ratio up to 7:3. Particleboards made with the sprayable adhesive have

acceptable strength attributes, and decreasing the mixture to as low as 20% soy flour produces boards with comparable strength and water resistance as those made with only PF (63, 64). PF has been described as the primary crosslinking agent in the previously cited patents, and similar work has been conducted by others. Wescott *et al*. (65) reported that soy based adhesives containing PF and 50-66% soybean flour were stable at room temperature for 100 days with no separation and maintained viscosity between 300-600 cps. Petroleum derived phenol amounts in these resins are approximately 75% lower than pure PF resins. Strandboard produced from the soy based resin performed similarly to PF only, and when 10% methylene diphenyl-isocyanate (MDI) was added to the soy based adhesive, thickness swell after 24-h soaking was 50% lower than that observed with PF only (65). Adhesive viscosity can be an issue in blended adhesives as well. Gel permeation chromatography has been used to determine optimal conditions for alkali treatment of soy flour blended with PF. Treating for <1 h at <100°C and pH 9-12 produced a modified soy flour with degraded components that are stable in adhesive formulations and do not lead to increased viscosity after blending (66).

Another blended resin system is comprised of SPI and Kymene®. Kymene® is a commercial wet-strength agent for paper also known as a polyamide-epichlorohydrin (PAE) adhesive resin. Kymene® is multi-functional and undergoes a series of reactions depending on processing conditions. Lap-shear tests made with cherry wood veneer indicate SPI blended with Kymene® produces adhesive bonds similar in strength to PF-only resin, but are less water resistant (67). One additional benefit of high importance to the industry using SPI-Kymene® is being

free of formaldehyde. The elimination of all formaldehyde is a key factor in commercial viability for future adhesive products because of growing concerns over carcinogenic compounds. Despite the benefits, the challenges to using SPI-Kymene® systems are low solids content, relatively long press times, and use expensive SPI in order to maximize adhesive characteristics.

Foaming adhesives. In most cases, viscosity is the primary physical characteristic measured for soy protein used as adhesives. The viscosity of soy protein dispersions does not increase linearly with increasing soy protein, but rather increases drastically when soy protein concentration is above 30 wt% (11). Soy protein adhesives can also be used in foam adhesive applications for plywood manufacture. Plywood adhesives are typically extruded and foamed at the time of application. Spray-dried blood protein is a standard part of plywood adhesive formulations. Hojilla-Evangelista (68) replaced blood protein with soy flour, SPI and SPC in foamed PF formulations. All soy products produced adhesives with foaming and strength properties at least equal to those of blood protein. Hojilla-Evangelista (69) demonstrated soy flour with the least amount of protein denaturation performed best in functional tests for foam adhesives. Surface hydrophobicity increased as soy proteins were denatured, and has been shown to increase foam volume (70, 71). Surface hydrophobicity does not correlate to foam stability however, and therefore does not have an appreciable meaning for the use of soy protein in foam adhesives (72, 73). Oil is a defoaming agent, so residual oil in soy protein products is a hindrance in foam extrusion adhesives (19). Foam volume and stability are

both essential functional characteristics for foam adhesives. Concerns with using animal blood in products are eliminated with extruded, foamed soy flour as well as lower product costs for soy flour relative to spray-dried animal blood.

Miscellaneous adhesives. Soy protein has been used in adhesive applications other than plywood, although at significantly smaller usage levels (42). SPI has been used in tacky and remoistening adhesives. SPI was used in formulating glue for shotgun shell casings in the late 1940's and early 50's due to its initial tack and superior water resistance compared compared to soy flour (74). A process was also patented for using an alkaline dispersion of soy flour as a binder for charcoal briquettes (42). Briquettes formulated with a soy flour dispersion along with other chemicals were resistant to weathering and breakage during handling. These utilization methods no longer exist, but continue to show the versatility and potential of soy protein as adhesives.

Summary

Soy protein is an abundant, renewable polymer with a history of use in the wood adhesives industry. The functional properties of soy protein allow for a variety of potential uses and modifications to fit into a variety of adhesive systems. For use in adhesive systems, soy flour almost certainly requires modification to alter functional properties, such as adhesive strength and to decrease viscosity, in order to enhance application properties. Protein hydrolysis and cross linking soy with other adhesives are the most common techniques for current soy protein adhesive

research. A limited amount of research has been carried out on enzymatic modifications for soy flour used in adhesives, and the array of enzymes possible for use in preparing adhesive systems has great potential for making a functional soy flour for use in multiple wood adhesives.

References

(1) Golbitz, P., 2008. Statistics. *Soya & Oilseed Bluebook*. Soyatech LLC: Bar Harbor, ME, p345-390.

(2) Anon. Bean Blast. Time, Oct. 21, 1935. pp. 34.

(3) Spon, W.; Spon, F.N., 1980. In Span's Encyclopedia of the Industrial Arts, Manufacturers, and Commercial Products. New York. p1378, 1814.

(4) Shurtleff, W., Aoyagi, A., 1997. In Shurtleff (ed), *Henry Ford and His Researchers' Work with Soybeans, Soyfoods, and Chemurgy – Bibliography and Sourcebook*. Soyfoods Center; Lafayette, CA.

(5) Montgaudry, B., 1955. Bulletin de la. Societe d'Acclimatation. 2, 16.

(6)Hance, H.F., 1918. Gard. Chron. 13,209.

(7) Pearson, A.M., 1984. Soy Proteins, In "Development in Food Proteins-II." B.J.F Hudson ed. Elseveir Applied Science Publisher. New York, NY.

(8) Bain, W., Circle, S., Olson, R., 1961. Synthetic and Protein Adhesives for Paper Coating. TAPPI Monograph Ser. No. 22. Technical Assoc. Pulp and Paper Inc. New York, NY.

(9) De, S.S., 1979. Technology of production from soybeans. FAO Agricultural Service Bulletin. Rome, Italy.

(10) Lusas, E.W., Riaz, M.N., 1995. Soy protein products: processing and use. J. Nutri. 125, 573-580.

(11) Wolf, W.J., 1970. Soy proteins: Their functional, chemical, and physical properties. J. Agr. Food Chem. 18, 969-976.

(12) Kinsella, J.E., 1979. Functional properties of soy proteins. J. Am. Oil Chem. Soc. 56, 242-258.

(13) Berg, J.M., Tymoczko, J.L., Stryer, L., 2002. Biochemistry 5th ed. W.H. Freeman and Co. New York, NY.

(14) Pine, S.H., Hendrickson, J.D., Cram, D.J., Hammond, G.S., 1980. Amino acids, peptide, and proteins. In "Organic Chemistry 4th Ed." McGraw-Hill Kogakusha, Ltd. Tokyo, Japan.

(15) Aspinall, F.O., Begbie, R., McKay, J.E., 1967. Polysaccharide components of soybeans. Cereal Sci. Today. 12, 223-261.

(16) Lusas, E.W., Rhee, K.C., 1995. Soy protein processing and utilization. In "Practical Handbook of Soybean Processing ad Utilization." D.R. Erickson ed. AOCS Press. Champaign, IL.

(17) Damodaran, S., Paraf, A., 1997. Food proteins and their applications. Marcel Dekker, Inc., New York, NY.

(18) Vojdani, F., Whitaker, J.R., 1994. Chemical and enzymatic modification of proteins for improved functionality. In "Protein Functionality in Food System." N.S. Hettiarachchy and F.R. Ziegler eds. Marcel Dekker, Inc., New York, NY.

(19) Lambuth, A.L., 1977. Soybean glues. In "Handbook of Adhesives." I. Skeist ed. Nostrand Reinhold Co., New York, NY.

(20) Feeney, R.E., Whitaker, J.R., 1977. Improvement through chemical and enzymatic modifications, ACS Symposium Ser. 160, Am. Chem. Soc. Washington, DC.

(21) Wu, Y.V., Inglet, G.E., 1974. Denaturation of plant proteins related to functionality and food applications. A Review. J. Food Sci. 39, 218-225.

(22) Thames, S.F., 1994. Soybean polypeptide polymers. In "Identifying New Industrial Uses for Soybean Protein." C.P. Baumel, C.P., L. Johnson, and C.A. Greiner eds. Special Report 95. Iowa State Univ. Ames, IA.

(23) Huang, J.C., 1994. The production of textile from soy proteins. Ph. D. Dissertation. Iowa State Univ., Ames, IA.

(24) Smith, A., Circle, S., 1972. Protein products as food ingredient. In "Soybeans: Chemistry and Technology, Vol. 1." A.K. Smith and S.J. Circle eds. Westport, CN.

(25) Sun, X., Bian, K., 1999. Shear strength and water resistance of modified soy protein adhesives. J. Am. Oil Chem. Soc. 76, 977-980.

(26) Brother, G.H., Smith, A.K., Circle, J.J., 1944. Soybean protein resume and bibliographs, U.S. Depart. of Agri., Bur. of Agri. Chem. and Eng., Urbana, IL.

(27) Tanford, C., 1968. Protein denaturation. In “Advances in Protein Chemistry.” C.B. Anfinson, M.K. Anson, J.T. Edsall, and F.M. Richards eds. Academic Press, Inc., New York, NY.

(28) Nir, I., Feldman, Y., Aserin, A., Garti, N., 1994. Surface properties and emulsion behavior of denatured soy proteins. J. Food Sci. 59, 606-610.

(29) Nakai, S., 1983. Structure-function relationships of food proteins with an emphasis on the importance of protein hydrophobicity. J. Agr. Food Chem. 31, 676-683.

(30) Kella, N.K.D., Yang, S.T., Kinsella, J.E., 1989. Effects of disulfide bond cleavage on structureal and interfacial properties of whey proteins. *Ibid*. 37, 1203-1210.

(31) Chobert, J.M., Bertrand-Harb, C., Nicholas, M.G., 1988. Solubility and emulsifying properties of caseins and whey proteins modified enzymatically by trypsin. *Ibid*. 35.6, 883-892.

(32) Kuehler, C.A., Stine, C.M., 1974. Effects of enzymatic hydrolysis on some functional properties of whey protein. J. Food Sci. 39, 379-382.

(33) Milligan, B., Holt, L.A., 1977. The complete enzymatic hydrolysis of crosslinked proteins. In “Advances in Experimental Medicine and Biology V.” M. Friedman ed. Plenum Pres. New York, NY.

(34) Hill, L.R., 1965. Hydrolysis of proteins in advances. In “Protein Chemistry.” C.B. Anfinsen, M.L. Anson, J.Tedsall, F.M. Richards eds. Academic Press, New York, NY.

(35) Feeney, R.E., 1980. Overview on the chemical deteriorative changes of proteins and their consequences. In “Chemical Deteriorative Changes of proteins.” J.R. Whataker, I. Fujimaki eds. ACS Symp. Series 123, ACS. Washington D.C..

(36) Wu, W.U., Hettiarachchy, N.S., Qi, M., 1998. Hydrophobicity, solubility, and emulsifying properties of soy protein peptides prepared by papain modification and ultrafiltration. J. Am. Oil Chem. Soc. 75, 845-850.

(37) Kim, S.Y., Park, P.S.W., Rhee, K.C., 1990. Functional properties of proteolytic enzyme modified oy protein isolate. J. Agr. Food Chem. 38, 651-656.

(38) Hettiarachchy, N.S., Kalapathy, U., Myers, D.J., 1995. Alkali-modified soy protein with improved adhesive and hydrophobic properties. J. Am. Oil Chem. Soc. 72, 1461-1464.

(39) Kalapathy, U., Hettiarachchy, N.S., Myers, D.J., Hanna, M.A., 1995. Modification of soy proteins and their adhesive properties on wood. *Ibid*. 72, 507-510.

(40) Johnson, 0., 1928. Process of treating soya beans. U.S. Patent 1,680,264.

(41) Laucks, I.F., Davidson, G., 1928. Vegetable glue and method of making the same. U.S. Patent 1,691,661.

(42) Burnett, R.S., 1951. Soybean protein industrial products. In: Markley, K.S. ed, *Soybeans and Soybean Products*, vol. 2. Interscience Publishers; New York.

(43) Schultz, J., Nardin, M., 1994. Theories and mechanisms of adhesion. In: Pizzi, A., Mittal, K.L. ed, *Handbook of Adhesive Technology*. Marcel Dekker, New York, NY.

(44) Feeney, R.E., Whitaker, J.R., 1985. In: Altschul, A.M., Wilcke, H.L. ed, *Chemical and Enzymatic Modification of Plant Proteins in New Protein Foods*. Academic Press.

(45) Kalapathy, U., Hettiarachchy, N.S., Rhee, K.C., 1997. Effect on drying methods on molecular properties and functionalities of disulfide bond cleaved by soy proteins. J. Am. Oil Chem. Soc. 74, 195-199.

(46) Lambuth, A.L., 1994. Protein adhesives for wood. In: Pizzi, A., Mittal, K.L. ed, *Advanced Wood Adhesive Technology*. Marcel Dekker Inc, New York, NY.

(47) Barth, B.P., 1977. Phenolic Resin Adhesives. In: Skeist, I. ed, *Handbook of Adhesives*, 2nd ed. New York, NY.

(48) Zhong, Z., Sun, X.S., 2001. Properties of soy protein isolate/polycaprolactone blends compatalized by methylene diphenyl diisocyanate. Polymer. 42, 6961-6969.

(49) Shera, J.N., Rawlins, J.W., Thames, S.F., 2007. Characterization of enzyme-modified soy protein isolate. Abstracts of Papers, 233rd ACS National Meeting. Chicago, IL.

(50) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by urea and guanidine hydrochloride. J. Am. Oil Chem. Soc. 77, 101-104.

(51) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. *Ibid*. 77, 705-708.

(52) Bian, K., Sun, X.S., 1998. Adhesive performance of modified soy proteins polymers. Polym Prepr (Am Chem Soc, Div Polym Chem). 39, 72-73.

(53) Klemazewski, J.L., Kinsella, J.E., 1991. Sulfitolysis of whey proteins: Effect on emulsion properties. J. Agr. Food Chem. 39, 1033-1035.6.

(54) Kalapathy, U., Hettiarachchy, N.S., Myers, D.J., Rhee, K.C., 1996. Alkali modification of soy proteins: effects of salts and disulfide bond cleavage on adhesion and viscosity. J. Am. Oil Chem. Soc. 73, 1063-1066.

(55) Liu, Y., Li. K., 2002. Chemical modification of soy protein for wood adhesives. Macromol. Rapid Comm. 23, 739-742.

(56) Lambuth, A.L., 2001. Blood and casein glues. In: Satas, D., Tracton, A.A. ed, *Coatings Technology Handbook*. Marcel Dekker Inc, New York,NY.

(57) Brown, O.E., 1987. Labeling adhesives. U.S. Patent 4,675,351.

(58) Zhao, K., Hao, X.F., Liu, D.J., 2000. Soy protein isolate composite adhesive. Zhengzhou Gongye Daxue Xuebao. 21, 15-18.

(59) Kreibich, R.E., 1995. New adhesives based on soy protein. Oils–Fats–Lipids 1995. Proc. 21st World Congr. Int. Soc. Fat Res. P.J. Barnes & Assoc., Bridgwater, UK.

(60) Karcher, L.P., 1997. The incorporation of corn and soybean based materials into plywood adhesives. Diss. Abstr. Int. B 57, 7297.

(61) Steele, P.H., Kreibich, R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy based adhesives. Adhes. Age. 41, 49–56.

(62) Clay, J.D., Vijayendran, B., Moon, J., 1999. Rheological study of soy-protein-based PRF wood adhesives. Annu. Tech. Conf. Soc. Plast. Eng. 57th.

(63) Kuo, M.L., Myers, D.J, Heemstra, H., Curry, D., Adams, D.O., Stokke, D.D., 2001. U.S. Patent 6,518,387.

(64) Kuo, M.L., Myers, D.J, Heemstra, H., Curry, D., Adams, D.O., Stokke, D.D., 2003. U.S. Patent 6,306,997.

(65) Wescott, J.M., Traska, A., Frihart, C.R., Lorenz, L., 2005. Durable soy based adhesive dispersions. In: Frihart, C.R. ed, *Wood Adhesives 2005*. San Diego, CA.

(66) Lorenz, L., Frihart, C.R., Wescott, J.M., 2007. Chromatographic analysis of the reaction of soy flour with formaldehyde and phenol for wood adhesives. J. Am. Oil Chem. Soc. 84, 769-776.

(67) Li, K., Peshkova, S., Geng, X., 2004. Investigation of soy protein-Kymene adhesive systems for wood composites. *Ibid*. 81, 487-491.

(68) Hojilla-Evangelista, M.P., 2002. Adhesive qualities of soybean protein-based foamed plywood glues. *Ibid*. 79, 1145-1149.

(69) Hojillia-Evangelista, M.P., Dunn, L.B., 2001. Foaming properties of soybean protein-based plywood adhesives. *Ibid*. 78, 567-572.

(70) Kinsella, J.E., Phillips, L.G., 1989. Structure:Function relationships in food protein, film and foaming behavior. In “Food Proteins.” J.E. Kinsella, W.G. Soucie ed, Am Oil Chemists’ Society, Champaign, Il.

(71) Hayakawa, S., Nakai, S., 1985. Relationships of hydrophobicity and net charge to the solubility of milk and soy proteins. J. Food Sci. 50, 486-491.

(72) Townsend, A., Nakai, S., 1983. Relationships between Hydrophobicity and foaming characteristics of food proteins. *Ibid*. 48, 588-594.

(73) Little Inc., A.D., 1951. Marketing Potential for Oilseed Proteins in. Industrial Uses, USDA Technical Bulletin 1043.

CHAPTER 2

Hydrolyzed soy flour and protein isolate in medium density fiberboard applications

A paper to be submitted to *Industrial Crops and Products*

J.F. Schmitz and D.J. Myers

Abstract

Blends of enzyme hydrolyzed soy flour (SF) and soy protein isolate (SPI) with phenol formaldehyde (PF) containing 5, 10, 20, 40, and 60% soy solids were prepared in the lab and applied via atomized air to wood fiber. Medium density fiberboard bonded with the blended adhesive was produced and mechanical and durability tests were conducted according to ASTM standard methods. Increased soy content increased the modulus of elasticity (MOE), but no change in the force required for rupture (MOR) was observed. Internal bond strength and durability (water resistance) decreased with increased SF or SPI content in blended adhesives. Durability was significantly less for SF compared to SPI blends. All soy/PF blends met or exceeded the national standards for interior-grade applications, except 60% SF in the 24-h soak test.

Key words: soy protein isolate, soy flour, soy hydrolysates, soy adhesives, protein adhesives, biocomposites

Introduction

Biobased adhesives have long played a role in the wood products industry, although their current impact is negligible. Caustic treated soybean meal was the mainstay of plywood adhesives from their emergence in the late 1920's through the 1950's (1-3). Peak soybean adhesive usage occurred in 1956 at approximately 45M kg (4). The decline of natural adhesives was popularly attributed to lower durability, shorter pot life, and less consistent properties and product quality in comparison to the newly available, petroleum derived adhesives.

Due to recent trends in natural products, rural economic development, and "green" chemistry, research in soy based adhesives has been reestablished. Initial efforts in the resurgence of soy adhesive research focused on using soy protein isolates (SPI). SPI modified with either alkali or protease enzyme trypsin, significantly improved adhesive strength and durability (5, 6). Numerous studies examined the effects of different denaturants on SPI. SPI denatured with sodium dodecly sulfate, guanidine hydrochloride, urea, and gluteraldehyde all increased the adhesive mechanical strength when compared to unmodified commercial SPI (7-9).

Most adhesive systems formulated with SPI are cost prohibitive relative to petroleum derived resins however, because SPIs generally sell for more than $2/kg. Steele *et al*. (10) developed a 50% isolate and 50% phenol-resorcinol-formaldehyde (PRF) cold-setting resin that was used in commercial finger-jointed lumber (Honeymoon System). Soy protein isolate utilized in the Honeymoon System was economical however, because PRF is a more costly adhesive compared even to other petroleum derived resins.

Kuo *et al*. (11, 12) demonstrated soy flour could be modified with a sodium hydroxide treatment and up to 70% soy solids could be crosslinked with PF. The resulting fiberboards had acceptable strength and durability properties in comparison to pure PF. A similar study by Hse *et al*. (13) showed that crosslinked soy/PF resins in a 7:3 ratio for oriented strand board had comparable internal bond (IB) strength, but lower durability than those made with commercial PF. Soy/PF blends used to make southern pine plywood compared favorably to traditional PF exterior plywood resins (14). Wescott *et al*. (15) reported soy based adhesives containing PF and 50-66% soybean flour were stable at room temperature for 100 days with no separation due to settling and a viscosity between 300-600 cps. Phenol amounts in these resins were approximately 75% lower than pure PF resins. Strandboard produced from soy based resin performed similarly to pure PF, and when 10% methylene diisocyanate was added to the soy based adhesive, thickness swell after a 24-h soak was 50% lower than that observed from the pure PF. Recent work has also examined natural foaming properties of soy flour in plywood adhesives applications. Foamed plywood adhesives made with soy material actually performed better when the soy component was flour or protein concentrate compared to SPI (16, 17).

One possible limitation in using soy flour is decreased durability due to the water solubility of carbohydrate material. Some hypothesize the chemical structure and multiple hydroxyl groups present in carbohydrates allows for extensive crosslinking and therefore a well developed three-dimensional matrix. Conner et al. (18) demonstrated that PF in conjunction with 50% carbohydrates led to acceptable

dry and wet strengths in Douglas fir veneer panels. Additional studies indicate carbohydrate based adhesives could be formulated for gluing high moisture veneer products. Carbohydrate-phenol-resorcinol resins had 98% wood failure after a 2-h boil (19).

Incorporation of biorenewable sources into adhesive formulations is not without limitations. Chemical complexity and structures can limit potential uses, and clear distinctions between biobased components such as SF and SPI have not been studied in depth. Treatments to soy materials have either been targeted at protein denaturation (7, 8), modification of chemical groups (20), or random breakdown of all materials present (11, 12). Enzyme modifications permit controlled modifications, and when multiple enzymes are used, both carbohydrates and proteins can be modified to maximize adhesive performance properties.

Experimental Procedures

Resin Preparation. HoneySoy90 (HS90), a defatted SF specified with 90 protein dispersibility index (PDI), was procured from Cenex Harvest States in Mankato, MN. With HS90 as the initial feedstock, SPI was made according to the lab scale procedure of Deak and Johnson (21). Proximate analyses of both HS90 and SPI are shown in Table 1.

SF and SPI dispersions with 25% solids were adjusted to pH 8.0 with 1.0 N sodium hydroxide. Dispersions were stirred at 150 rpm and brought to 50°C in a heated water bath. After 20 min at constant temperature, dispersions were treated

with a 0.25% (w/v) dosage of Protex 89L (Genencor Intl.), a bacterial serine endopeptidase derived from a genetically modified strain of *Bacillus subtilis*. Ideal processing conditions for Protex 89L activity are 50°C and pH 8.0, and the enzyme can be inactivated by holding for 5 minutes at 80°C. The hydrolysis reaction was allowed to continue for 3 h after which point degree of hydrolysis (DH) no longer changed. DH was measured using methods described by Nielsen *et al.* (22). The measured degree of hydrolysis was 25% and 26% for SPI and SF hydrolysate, respectively. Bulk soy protein hydrolysate was sealed in 1 liter bottles and stored at -20°C until time of use.

PF was synthesized in the lab with a 2.4:1 molar ratio of formaldehyde:phenol and a 0.1:1 molar ratio of sodium hydroxide:phenol. Materials were mixed in a 3-arm flask equipped with a condensation column and temperature probe. PF was compounded in a 3-stage reaction (60°C for 90 min, 75°C for 30 min, and finally 95°C for 60 min). Once cooled the PF was adjusted to a final pH of 10.2 using 2.0 N sodium hydroxide. Final solids content of PF resin was 50.7%. Bulk PF was stored at 4°C until time of use.

Resin blends were prepared at the time of use with 5, 20, 35, and 50% of total solids as SF or SPI hydrolysates. The resin blends were adjusted to pH 10.2 using 1.0 N sodium hydroxide and then mixed for 30 min at 70°C.

Fiberboard Fabrication and Evaluation. Medium density fiberboard (MDF) was manufactured with pinewood fiber procured from Jeld-Wen, Inc. (Dubuque, IA). Prior to use, pinewood fiber was oven dried in a 180°C oven to about 2% moisture.

For each sample replicate sufficient fiber to make three 41 cm x 41 cm x 1.3 cm MDF boards at a target density of 80 g/cm^3 was placed into a tumbler. Soy/PF resins were atomized and sprayed onto the fiber at 8% application rate based on dry fiber weight. Following the completion of adhesive spraying plus an additional 2 min of tumbling, fiber was removed from the tumbler with the aid of a vacuum/blower to fluff the fiber.

The fiber was hand-laid into a 41 cm x41 cm forming box and prepressed. Boards were pressed with a 16 MPa hydraulic press from Wabash MPI (Wabash, IN) with sufficient pressure to allow closing within 15 sec. All boards were pressed with an 8 min press cycle at 200°C and 5.3 MPa. Post curing of fiberboards was done at ambient conditions in stacks of 10 fiberboards wrapped in muslin bags for 36 h.

Sample preparation and testing procedures were performed in accordance with ASTM Standard Method D1037-99 (23). Fiberboards were trimmed to 35.6 cm x 35.6 cm specimens and further prepared as outlined in Figure 1 for static bending (modulus of elasticity [MOE], modulus of rupture [MOR]) and strength perpendicular to surface (IB) testing. Static bending was performed on a 3-point bending setup with a 30 cm span. Dimensional stability samples of 7.6cm x 10.2cm were obtained from bending test specimens after failure. Dimensional stability samples were conditioned at 65% relative humidity and 23°C for five days prior to testing. The ambient temperature in the laboratory for the 24-h soak test was 23°C. The 2-h boiling tests were done with 36 samples chosen randomly at a time in a covered, boiling water bath. Weight and thickness were measured before and after the tests

to calculate water absorption and thickness swell. Dimensional stability tests were measured as percent thickness swell after 2 h boiling (TS-2B) and 24 h soaking (TS-24S) in distilled water. Following the 2-h boil measurements, samples were dried and residual IB specimens (IB-B) were obtained. Static bending and IB measurements were performed by using an MTI Phoenix Ultimate Testing Machine from Measurements Technology, Inc. (Roswell, GA). Board density was calculated from dimensional measurements and total mass of the MOE/MOR specimens from each board.

Experimental Design and Analysis. Three replicates of enzyme hydrolysates were produced in the lab and blended with one bulk batch of PF resin. With each batch 3 MDF boards were made for all treatments. Data was subjected to Analysis of Variance (ANOVA) using the general linear model (GLM) procedure by the Statistical Analysis Software Program version 9.1 (SAS Institute, Inc., Cary, NC). Statistical significance was based on $p < 0.05$.

Results and Discussion

Among the types of hydrolysate and replacement levels there were no significant differences in board density. This was important because it confirmed the MDF fiber/resin mats were consistently assembled and pressed. Two types of measurements were made on the MDF boards. The first are characterized as dry mechanical properties. Table 2 shows the static bending properties. MOE is the

numerical description of an object's tendency to deform under stress and MOR is the maximum stress required to cause fracture. Both are dependent on sample dimension, density, and adhesive bond strength, hence the importance of uniform board density. There were no significant differences in MOR between boards prepared with SF and SPI, but as the percentage of soy in the resin increased, MOE of MDF increased. In this MDF application the maximum force to fracture was not significantly different, and therefore use of soy in the resin did not impact the maximum stress the MDF could withstand. No differences were observed for MOR between either soy component compared to pure PF, or with increasing amounts of soy in the resin. As shown in Table 2, the MOE and MOR for MDF made from both SF and SPI exceeded the minimum standard ($2.4x10^3$ and 24.0 MPa respectively) for the American National Standard Institute (ANSI) standards for interior grade MDF (24). The lowest MOE among treatments with soy/PF blends was $3.7x10^3$ MPa for 5% soy and for MOR it was 36.2 MPa with 60% soy in the resin blend.

IB is a measure of the perpendicular force required to cause failure in MDF. Similar to MOE, significant differences were observed among the IB samples, with increasing percentage of soy in the resin causing a decrease in IB. Both SF and SPI treatments exhibited decreasing IB values as soy level increased. At 5% replacement there were no differences in IB among any resin blend. At replacement levels >5% however, all treatments were statistically different from PF (0% soy), and the IB of SPI was significantly lower than that of SF. Table 3 defines the observed IB values and show where statistical differences existed with increased soy content. While increased soy content in the resin differed from the

control PF resin, the average IB value for 60% soy replacement of both SF and SPI still exceeded the ANSI standard of 0.60 MPa. Residual IB (IB-B) after 2-h boil test, showed a dramatic difference relative to the initial, dry IB values. IB-B with soy in the resin corresponded to a significant drop in wet strength. Incorporation of even 5% SF or SPI decreased IB-B strength compared to the control PF. Additionally, significant interaction was observed between the factors of soy component and replacement level, with IB-B from SF being lower than SPI.

Also included in Table 3 are results from durability testing (TS-2B and TS-24S). In all cases, water absorption was proportional to the thickness swell. There was no significant difference among the mean TS-24 values, and all means except the 60% SF were below the ANSI MDF standard for maximum swell (10%). PF resin blends with soy were no less durable and susceptible to expansion and water accumulation than MDF made with pure PF. There was a significant statistical interaction present among the TS-2B samples. Increased levels of both SF and SPI increased average thickness swell. The addition of soy into the resin and MDF matrix compromised product durability. Soy component and replacement level demonstrated a significant interaction with SF swelling more than SPI as replacement level increased. With the only difference between the two formulations being the protein content and soy composition, we speculate the more soluble carbohydrate fraction in SF contributed to the increased water absorption and swelling.

Conclusions

With the variety of research being conducted on soy protein adhesives, very few compare the resin quality when using SF or SPI. Considering the large price differential between the two soy products, adhesive quality and characteristics between the two are important when considering industrial viability. This research shows that in a PF model system few significant differences are found between enzyme hydrolyzed SF and SPI. The ultimate force required to fracture MDF was not dependent on the amount of soy or the type of soy protein source used, but greater elasticity was observed in MDF made from resin that contained soy compared to pure PF. With 8% resin application, the internal bond strength of all MDF (up to 60% soy) met or exceeded the ANSI requirements for interior applications. While significant differences did exist in IB strength and thickness swell, measurements between MDF made with SF and SPI, both types of soy protein hydrolysates resulted in MDF that met or exceeded the ANSI standard for interior use when the resin contained as much as 40% soy component.

Acknowledgements

This work was supported by the USDA, CSREES grant 2006-34432-17128, and was performed in cooperation with Genencor International. The authors thank Phil Hellerud of Jeld-Wen, Inc., for supplying the wood fiber.

References

(1) Johnson, O., 1923. Process of treating soya beans. U.S. Patent 1,680,264.

(2) Laucks, I.F., Davidson, G., 1928. Vegetable glue and making of the same. U.S. Patent 1,691,661.

(3) Babcock, G.E., Smith, A.K., 1947. Extending phenolic resin plywood glues with proteinaceous materials. Ind. Engr. Chem. 39, 85-88.

(4) Lambuth, A.L., 1977. Soybean glues. In "Handbook of Adhesives," I. Skeist ed. Van Nostrand Reinhold Co., New York, NY.

(5) Hettiarachchy, N.S., Kalapathy, U., Myers, D.J., 1995. Alkali-modified soy protein with improved adhesive and hydrophobic properties. J. Am. Oil Chem. Soc. 72, 1461-1464.

(6) Kalapathy, U., Hettiarachchy, N.S., Myers, D., Hanna, M.A., 1995. Modification of soy proteins and their adhesive properties on woods. *Ibid*. 72, 507-510.

(7) Zhong, Z.K., Sun, X.S., Wang, D.H., 2004. Wet strength and water resistance of modified soy protein adhesives and effects of drying treatment. J. Polym. Environ. 11, 137-144.

(8) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. J. Am. Oil Chem. Soc. 77, 705-708.

(9) Sun, X., Bian, K., 1999. Shear strength and water resistance of modified soy protein adhesives. *Ibid.* 76, 977-980.

(10) Steele, P.H., Kreibich, R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy based adhesives. Adhes. Age. 41, 49–56.

(11) Kuo, M.L., Adams, D., Myers, D.J., Curry, D., Heemstra, H., Smith, J.L., Bian, Y., 1998. Properties of wood/agricultural fiberboard bonded with soybean-based adhesives. For. Prod. J. 48, 71-75.

(12) Kuo, M.L., Myers, D.J., Heemstra, H., Curry, D., Adams, D.O., Stokke, D.D., 2001. Soybean-based adhesive resins and composite products utilizing such adhesives. U.S. Patent 6,518,387.

(13) Hse, C.Y., Fu, F., Bryant, B.S., 2000. Development of formaldehyde-based wood adhesives with co-reacted pheno/soybean flour. In "Wood Adhesives 2000", Forest Products Society, Madison, WI.

(14) Yang, I., Kuo, M.L., Myers, D.J., 2006. Bond quality of soy based phenolic adhesives in southern pine plywood. J. Am. Oil Chem. Soc. 83, 231-237.

(15) Wescott, J.M., Traska, A., Frihart, C.R., Lorenz, L., 2005. Durable soy based adhesive dispersions. In "Wood Adhesives 2005", Forest Products Society, Madison, WI.

(16) Hojilla-Evangelista, M.P., Dunn Jr., L.B., 2001. Foaming properties of soybean protein-based plywood adhesives. J. Am. Oil Chem. Soc. 78, 567-572.

(17) Hojilla-Evangelista, M.P., 2002. Adhesive qualities of soybean protein-based foamed plywood glues. *Ibid.* 79, 1145-1149.

(18) Conner, A.H., Lorenz, L.F., River, B.H., 1989. Carbohydrate-modified phenol formaldehyde resins formulated at neutral conditions. In "Adhesives from Renewable Resources," ACS Symposium Series 385. American Chemical Society, Washington, D.C.

(19) Karchesy, J.J., Clark, R.J., Helm, R.F., Ghoudoussi, V., Krahmer, R.L., 1989. Fast-curing carbohydrate-based adhesives. In "Adhesives from Renewable Resources," ACS Symposium Series 385. American Chemical Society, Washington, D.C.

(20) Liu, Y., Li, K., 2002. Chemical modifications of soy protein for wood adhesives. Macromol. Rapid Comm. 23, 739-742.

(21) Deak, N.A., Johnson, L.A., 2006. Effects of extraction temperature and preservation method on functionality of soy protein. J. Am. Oil Chem. Soc. 84, 259-268.

(22) Nielsen, P.M., Petersen, D., Dambmann, C., 2001. Improved method for determining food protein degree of hydrolysis. J. Food Sci. 66, 642-646.

(23) American Society of Testing and Materials, 1999. Standard test method for evaluating properties of wood-base fiber and particle panel materials. Designation: D1037-99. West Conshohocken, PA, pp. 142-171.

(24) American National Standard Institute, 2002. Medium density fiberboard (MDF) for interior applications. ANSI A208.2-2002. Composite Panel Association, Gathersburg, MD.

Table 2-1. Proximate composition of soy components[1]

Constituent	HS90	SPI
Protein	53.0	90.3
Fat	3.5	1.0
Ash	7.1	3.8
Carbohydrates	36.4	4.9

[1] Measurements on a moisture-free basis

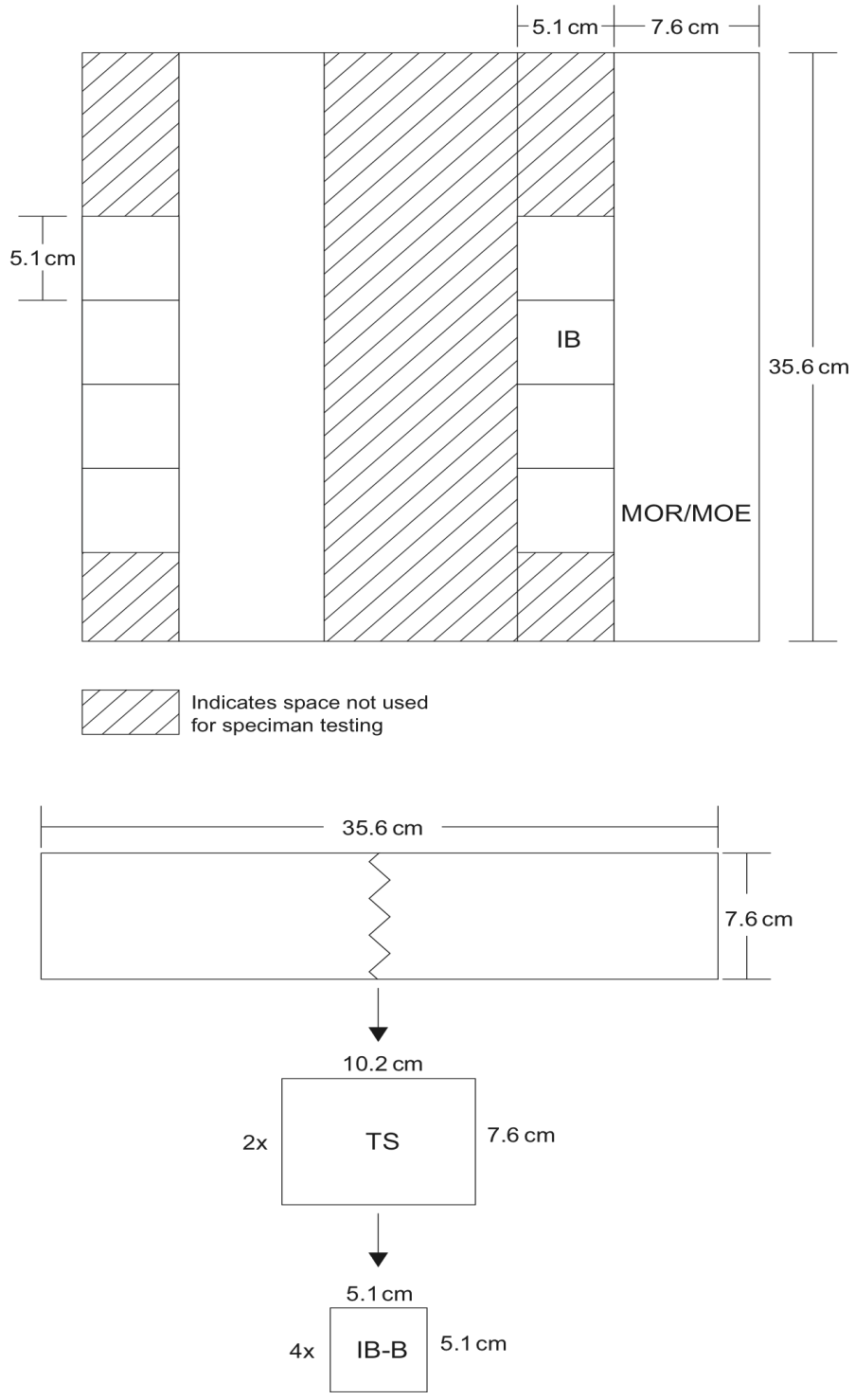

Figure 2-1. MDF testing specimen diagram

Table 2-2. Static bending properties for soy resin blends

Resin Properties		Static Bending Properties			
Soy component	% Soy	MOE MPa x10[3]		MOR MPa	
SPI	5	3.71		36.6	
SF	5	3.73		37.3	
Average[1]		3.72	b[2]	37.0	a
SPI	10	3.78		36.4	
SF	10	3.76		37.4	
Average		3.77	b	36.9	a
SPI	20	3.90		36.0	
SF	20	3.85		37.1	
Average		3.87	b	36.5	a
SPI	40	4.07		36.3	
SF	40	4.05		36.4	
Average		4.06	c	36.4	a
SPI	60	4.30		35.8	
SF	60	4.23		36.6	
Average		4.26	d	36.2	a
PF	- - -	3.50	a	36.1	a
ANSI Standard, MDF[3]		2.40		24.0	

[1] No significant difference existed between SPI and SF at the $p < 0.05$ level.

[2] Means in columns with common letters were not significantly different at the $p < 0.05$ level.

[3] American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

Table 2-3. Perpendicular strength and durability properties

Resin Composition		Fiberboard Properties							
Soy Component	% Soy	IB Mpa		IB-B Mpa		TS-2B (% swell)		TS-24S (% swell)	
SPI	5	1.05	a	0.78	b	9.1	a	7.9	a
	10	1.01	a	0.74	b	9.7	a	8.0	a
	20	0.96	a,b	0.68	b,c	10.5	a,b	8.8	a
	40	0.85	b	0.56	c	11.7	b	9.3	a
	60	0.77	c	0.50	d	12.7	c	9.7	a
SF	5	1.01	a	0.79	b	9.2	a	8.1	a
	10	0.90	b	0.74	b	9.8	a	8.4	a
	20	0.85	b,c	0.55	c	11.4	b	8.7	a
	40	0.74	c,d	0.47	c	13.8	c	9.3	a,b
	60	0.68	d	0.38	d	16.7	d	10.2	b
PF		1.09	a	0.93	a	9.2	a	7.9	
ANSI Standard, MDF		0.60		- - -		- - -		10.0	

[1] Means in columns with common letters were not significantly different at the 5% level within the type of soy component.

[2] American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

CHAPTER 3

Effects of degree of protein hydrolysis on soy flour/phenol formaldehyde adhesives

A paper to be submitted to *Industrial Crops and Products*

J.F. Schmitz and D.J. Myers

Abstract

The effects of the degree of protein hydrolysis and amount of soy flour in soy/phenol formaldehyde (PF) blends were determined in a medium density fiberboard (MDF) model system. MDF with 8% resin was prepared and tested according to ASTM standard methods. The modulus of elasticity increased with greater soy content in the resin matrix, but no significant effects were seen in the force required to fracture samples. Degree of protein hydrolysis (DH) had no effect on either elasticity or force to rupture. As soy content and DH increased, both factors resulted in decreased internal bond strength. Protein hydrolysis was beneficial for strong internal bonds in MDF, but complete protein hydrolysis of the soy flour led to decreased strength. Durability of MDF decreased with increasing DH.

Key words: soy flour, soy hydrolysates, soy adhesives, protein adhesives, natural adhesives, biocomposites

Introduction

During the years spanning 1930 through the mid-1960's biorenewable adhesives were prominent in the wood products industry. Natural adhesives from materials such as soy protein, carbohydrates, casein, and blood albumin produced materials with sufficient properties to meet the demands of consumers and industry throughout World War II. Soy protein adhesives peaked in 1956 with approximately 45 million kg of annual use (1). Through three decades the basic technology of natural adhesives remained the same as described in an early patent where adhesive properties of soy flour (SF) were improved by dispersing in strong alkali (2). Alkaline treatment caused denaturation of the proteins, exposing more polar amino acid residues and thereby increasing the adhesion of SF with polar wood molecules. The major downfall of early SF adhesives was the lack of water resistance. Additional chemical compounds were added, such as calcium hydroxide or sodium silicate, to increase water holding capacity and stabilize viscosity (2). In the later stages of soy flour adhesive use, crosslinking agents became an important component in adhesive formulations. Compounds including, but not limited to, carbon disulfide, thiourea, and potassium xanthate, were used to increase water resistance and to stabilize the denatured structure from further hydrolysis (3).

Soy protein isolate (SPI) and SF are abundant commercial products that have been used to formulate adhesives for wood products in numerous approaches. The first resurgent use for soy adhesives was blending modified SF with traditional petroleum based adhesives. Kuo *et al*. (4) showed that up to 70% soy material

could be crosslinked with phenol formaldehyde (PF) and maintain mechanical properties. SPI or SF was also prereacted with phenol and then subsequently with formaldehyde to have soy/PF resins either used alone, or used in combination with a relatively small proportion of methylene diphenyl isocyanate (MDI) (5). In these adhesives, soy material is barely in the majority (up to 60%). Another coreacting approach is through the formation of an adduct of soy protein with maleic anhydride followed by hardening with poly(ethylimine) (6). Additional research studies have examined the characteristics of modified soy proteins as lone adhesives with varying results. Various chemicals, such as citric acid, urea, alkaline, and guanidine hydrochloride, have been used to improve bonding strength of soy based adhesive (7-10). The historical use of soy based adhesives was primarily in plywood (1), but resurgent efforts have also examined soy based adhesives to bond fiberboard (4, 10, 11), particleboard (12, 13), and finger-jointed lumber (14). Throughout all recent studies of soy based adhesives, a primary concern is still wet strength and durability (4-6, 8-10).

Based on the fore mentioned work, it is widely accepted that SF used in adhesive formulations requires modification to enhance adhesive properties. A common approach to all successful modifications is the exposure of more polar groups to enhance bonding with wood fiber, but a recurring issue has been the extent of modification has not been properly characterized (7-9, 11, 15). Enzymatic treatments of soy flour have the potential to modify flours in a similar manner as caustic treatments, but also offer the benefit of controlled modification. The use of enzymes can lead to tailored SF hydrolysates with different properties for different

applications. The present study evaluated the mechanical and durability effects of degree of hydrolysis (DH) on SF blended with PF in a medium density fiberboard (MDF) system.

Experimental Procedures

Resin Preparation. Defatted SF (HoneySoy90) was procured from Cenex Harvest States in Mankato, MN. Protein content was 53.0% and residual fat was 1.2% on a moisture free basis, with a specified protein dispersibility index of 90. SF dispersions with 25% solids were adjusted to pH 8.0 with 1.0 N sodium hydroxide. Dispersions were stirred at 150 rpm and brought to 50°C in a water bath. After 20 min at constant temperature, dispersions were treated with 0.10 wt% dosage of Protex 89L (Genencor Intl.). Protex 89L is a bacterial serine endopeptidase derived from a genetically modified strain of *Bacillus subtilis*. Ideal processing conditions for Protex 89L activity are 50°C and pH 8.0, and the enzyme can be inactivated by holding for 5 min at 80°C. Degree of hydrolysis (DH) was measured by the OPA method as described by Nielsen *et al*. (16). Hydrolysis was stopped at 5, 10, 18, and 26% DH. Following inactivation of the enzyme, samples were stored at -20°C until used.

PF was synthesized in the lab with 2.4:1 molar ratio of formaldehyde:phenol and 0.1:1 molar ratio of sodium hydroxide:phenol. Reactants were continuously mixed in a 3-arm flask equipped with a condenser column and temperature probe. PF was compounded in a 3-stage reaction, 60°C for 90 min, 75°C for 30 min, and finally 95°C for 60 min. Once cooled, PF was adjusted to a final pH of 10.2 using

2.0 N sodium hydroxide. Final solids content of the PF resin was 50.7%. Bulk PF was stored at 4°C until used.

Resin blends were produced at the time of use with 20, 40, and 60% soy solids in the resin blend. Resin blends were adjusted to pH 10.2 using 1.0 N sodium hydroxide, and then mixed for 30 min at 70°C before applying to wood fiber.

Fiberboard Fabrication and Evaluation. MDF was manufactured using pinewood fiber procured from Jeld-Wen, Inc. (Dubuque, IA). Prior to use, pinewood fiber was oven dried at 180°C to about 2% moisture. For each sample replicate, enough fiber to make three 41 cm x 41 cm x 1.3 cm MDF boards at a target density of 80 g/cm^3 was placed into a tumbler. SF/PF resins were atomized and sprayed onto the fiber at an 8% application rate based on dry fiber weight. Following the completion of adhesive spraying plus two additional minutes of tumbling, fiber was removed from the tumbler with the aid of a vacuum/blower to fluff the fiber. Fiber was hand-laid into a 41 cm x 41 cm forming box and prepressed. Boards were pressed with a 16 MPa hydraulic press from Wabash MPI (Wabash, IN) with sufficient pressure to allow closing within 15 sec. All boards were pressed with an 8-min press cycle at 200°C and 5.3 MPa. Post curing of fiberboards was done at ambient conditions in stacks of 10 fiberboards wrapped in muslin bags for 36 h.

Sample preparation and testing was performed according to ASTM Standard Method D1037-99 (17). Fiberboards were trimmed to 35.6 cm x 35.6 cm specimens and further prepared for static bending (modulus of elasticity [MOE] and modulus of rupture [MOR]) and strength perpendicular to surface (internal bond [IB])

testing. All mechanical strength attributes were measured by using an MTI Phoenix Ultimate Testing Machine from Measurements Technology, Inc. (Roswell, GA). Board density was calculated from dimensional measurements and total mass of the MOE/MOR specimens from each board. Static bending was performed on a 3-point bending setup with a 30 cm span. Figure 1 depicts the scheme used for cutting samples from the trimmed fiberboard. Dimensional stability samples, 7.6 cm x 10.2 cm in size, were obtained from the bending test specimens after failure. Samples were conditioned at 65% relative humidity and 23°C for five days prior to testing. The ambient temperature in the lab for the soaking procedure was 23°C. The 2-h boiling tests were done with 36 samples chosen randomly at a time in a covered, boiling water bath. MDF thickness was measured before exposure to water, and again 30 minutes after completion of each respective test. In accordance with the ASTM standard (17), thickness swell is reported in Table 2 as the percentage increase in thickness. Dimensional stability tests were measured as percent thickness swell after 2 h of boiling (TS-2B) and 24 h of soaking (TS-24B) in distilled water. Following the 2-h boil measurements, samples were dried and residual IB specimens were obtained (IB-B). For determining modulus of rupture and elasticity (MOR and MOE respectively), two samples per board were used. There were eight IB samples per board.

Experimental Design and Analysis. Three replicates of enzyme hydrolysates from HS90 were produced in the lab, and blended for use from one batch of bulk PF resin. All data was subjected to Analysis of Variance (ANOVA) using the general

linear model (GLM) procedure in the Statistical Analysis Software Program version 9.1 (SAS Institute, Inc., Cary, NC). Significant effects are reported based on $p<0.05$.

Results and Discussion

The density of all board samples fell into the range of 77.8-81.5 g/cm^3, meeting the target density of 80 g/cm^3. Table 1 represents the static bending results for MDF prepared with varied soy content in the resin and differing protein DH. Increasing soy content in the PF resin blend did not change the MOE or MOR with higher levels of soy flour in the resin system. The degree of protein hydrolysis had no significant factor on either MOE or MOR. Combining these results with those of the previous chapter, higher soy content in a resin system increases the MOE, but the extent of modification to the protein does not.

IB is the applied perpendicular force required to cause separation in the MDF. Results for IB analysis are given in Table 2. Similar to the MOR results, significant differences were observed for mean IB values between 20% soy and higher replacement levels (40 and 60%). Residual IB samples measured after the 2-h boiling test were significantly lower than the initial IB strength, but followed the same trend of decreased IB strength with higher soy content. Statistical analysis did not reveal any interaction between soy content and DH, but DH itself was a significant treatment factor in the designed experiment. Among all levels of soy content in the dry samples, increased DH led to higher IB values, but only up to 18% DH. At DH >26%, IB values declined to a value which was similar to the 5% DH within each respective soy content level. This result indicates that an optimum

peptide length exists for achieving high bond strength in PF resin blends. Too little hydrolysis and complete hydrolysis both led to decreased IB strength compared to intermediate hydrolysis. IB-B results showed that DH >10% was deleterious to MDF strength, but 10% DH was also significantly improved compared to the low level 5% DH.

The final class of testing on the MDF was durability tests in the form of 2-h boiling and 24-h soaking. Results from the 24-h soaking test did not indicate any significant differences among soy content or DH of the soy protein. The boiling procedure is a more rigorous test though, and significant differences were observed. Although both soy content and DH were significant factors, there was no interaction among the two factors. As soy content and DH increased, thickness swell increased. The finding that thickness swell increased with increasing soy content is consistent with results from the previous chapter and unpublished work from the same lab. Creating shorter peptides through hydrolysis decreased the durability of MDF with soy/PF resins.

Tables 1 and 2 also show the 2002 ANSI standard for interior grade MDF. The MOR and MOE minimum standards are 2.40×10^3 and 24.0 MPa respectively. Meanwhile the IB minimum standard is 0.60 MPa. With 8% applied resin, all MDF characteristics met the required standards. Both MOE and MOR were considerably higher with all treatment combinations than the ANSI standard value. Considering that IB decreased with increasing soy content and DH, even MDF with the highest soy content of 60% and highest DH of 26% was above the standard of 0.60 MPa.

For durability purposes only the 24-h soak has a standard, and the mean value of all treatments was below the 10.0% acceptable maximum thickness swell.

Conclusions

This work reports for the first time that MDF properties are affected by the extent of hydrolysis of the soy protein. No interaction of the DH or soy replacement level treatments were observed among any of the MDF properties, but notably DH affected the strength for internal bond. Partial protein hydrolysis was beneficial for IB strength, but above 18% a decrease was observed. In the more rigorous durability tests (2h boil), DH was deleterious to dimensional stability. MDF strength properties were maximized by partial hydrolysis, but there was an optimum level after which strength and durability properties were harmed.

Acknowledgements

This work was supported by the USDA, CSREES grant 2006-34432-17128 and was performed in cooperation with Genencor International (Rochester, NY). The authors express gratitude to Phil Hellerud of Jeld-Wen, Inc. (Dubuque, IA) for supplying the wood fiber.

References

(1) Lambuth, A.L., 1977. Soybean glues. In “Handbook of Adhesives,” I. Skeist ed. Van Nostrand Reinhold Co., New York, NY.

(2) Laucks, I.F., Davidson, G., 1928. Vegetable glue and making of the same. U.S. Patent 1,691,661.

(3) Bjorksten, J., 1951. Cross linkages in protein chemstry. In “Advances in Protein Chemistry,” Academic Press, New York, NY.

(4) Kuo, M.L., Adams, D., Myers, D.J., Curry, D., Heemstra, H., Smith, J.L., Bian, Y., 1998. Properties of wood/agricultural fiberboard bonded with soybean-based adhesives. For. Prod. J. 48, 71-75.

(5) Wescott, J.M., Frihart, C.R., Traska, A.E., 2006. High soy containing water durable adhesives. J. Adhesion Sci. Technol. 20, 859-873.

(6) Liu, Y., Li, K., 2002. Chemical modification of soy protein for wood adhesives. Macromol. Rapid Comm. 23, 739-742.

(7) Zhong, Z.K., Sun, X.S., Wang, D.H., 2003. Wet strength and water resistance of modified soy protein adhesives and effects of drying treatment. J. Polym. Environ. 11, 137-144.

(8) Sun, X.S., Bian, K., 1999. Shear strength and water resistance of modified soy protein adhesives. J. Am. Oil Chem. Soc. 76, 977-980.

(9) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. *Ibid.* 77, 705-708.

(10) Zhong, Z.K., Sun, X.S., Fang X.H., Ratto, J.A., 2002. Adhesive strength of guanidine hydrochloride – modified soy protein for fiberboard application. Int. J. Adhes. Adhes. 22, 267-272.

(11) Zhong, Z., Sun, X.S., 2001. Properties of soy protein isolate/polycaprolactone blends compatalized by methylene diphenyl diisocyanate. Polymer. 42, 6961-6969.

(12) Mo, X.Q., Hu, J., Sun, X.S., Karrab, G.S., 2001. Compression and tensile strength of low-density straw-protein particleboard. Ind. Crop Prod. 14, 1-9.

(13) Cheng, E.Z., Sun X.S., 2004. Adhesive properties of modified soybean flour in wheat straw particleboard. Compos. Part A-Appl S. 35, 297-302.

(14) Steele, P.H., Kreibich R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy based adhesives. Adhes. Age. 41, 49–56.

(15) Hojilla-Evangelista, M.P., Dunn Jr, L.B., 2001. Foaming properties of soybean protein-based plywood adhesives. J. Am. Oil Chem. Soc. 78, 567-572.

(16) Nielsen, P.M., Petersen, D, Dambmann, C., 2001. Improved method for determining food protein degree of hydrolysis. J. Food Sci. 66, 642-646.

(17) American Society of Testing and Materials, 1999. Standard test method for evaluating properties of wood-base fiber and particle panel materials. Designation: D1037-99. West Conshohocken, PA, pp. 142-171.

(18) American National Standard Institute, 2002. Medium density fiberboard (MDF) for interior applications. ANSI A208.2-2002. Composite Panel Association, Gathersburg, MD.

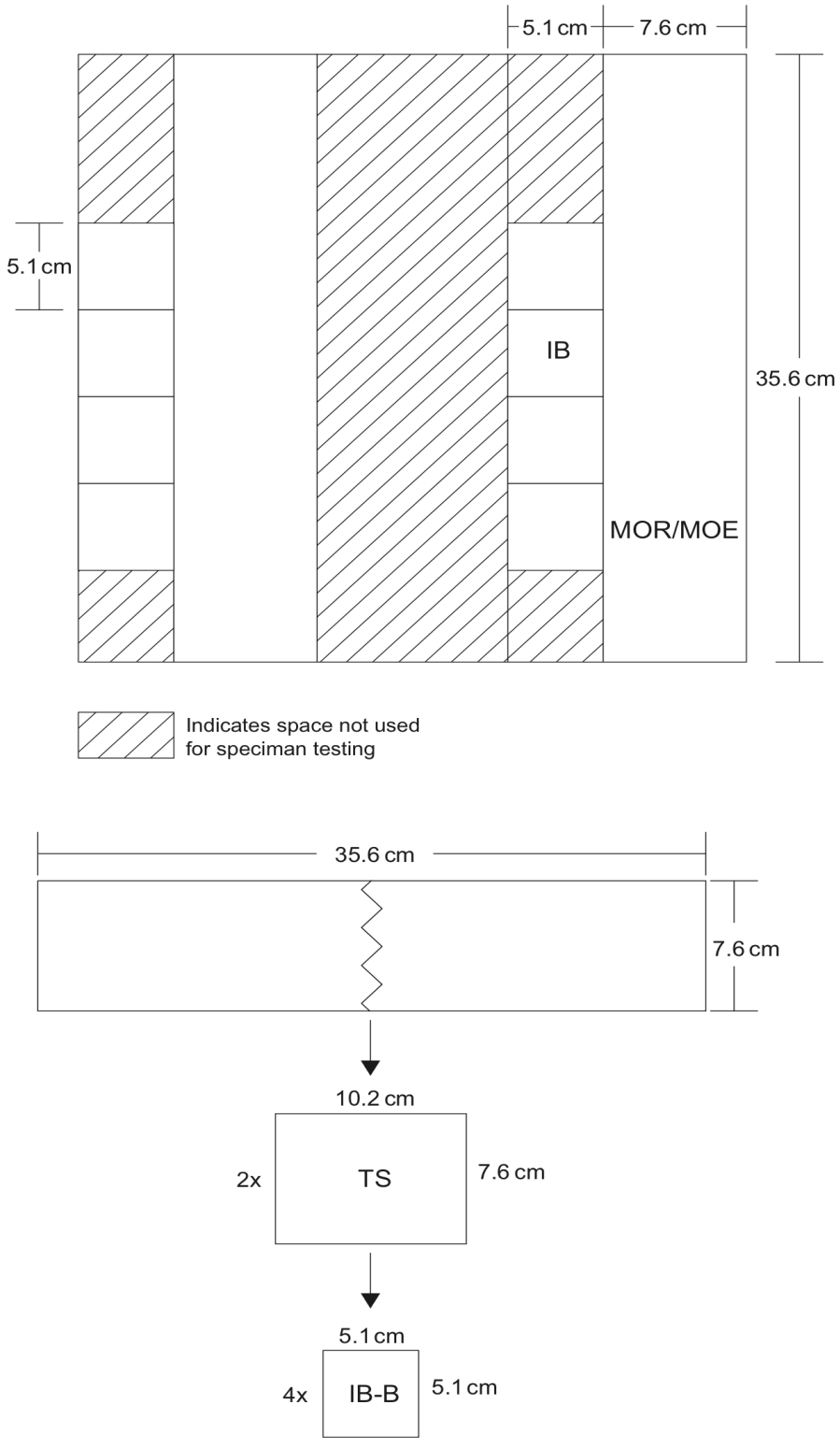

Figure 3-1. MDF testing specimen diagram

Table 3-1. Static bending properties for SF/PF resin blends

Soy %	DH	MOE x1000 MPa		MOR Mpa	
20	5	3.54		35.1	
	10	3.62		35.9	
	18	3.80		35.7	
	26	3.88		35.9	
Average		3.71	A	35.7	A
40	5	3.76		35.7	
	10	3.88		36.1	
	18	4.01		SF	
	26	4.12		35.7	
Average		3.94	B	35.8	A
60	5	3.97		36.1	
	10	4.07		35.9	
	18	4.22		36.1	
	26	4.34		SF	
Average		4.15	C	36.2	A
ANSI Standard, MDF		2.40		24.0	

[1] Means in columns with common letters were not significantly different at the 5% level.

[2] American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

Table 3-2. SF resin perpendicular strength and durability properties

Soy %	DH %	IB MPa		IB-B MPa		TS-2B % swell		TS-24S % swell	
20	5	0.82	a	0.72	a	9.1	a	8.6	a
	10	0.95	b	0.70	a	9.4	a	8.6	a
	18	0.90	b	0.63	b	10.5	b	9.0	a
	26	0.81	a	0.57	c	11.4	c	8.9	a
Average		0.87	A	0.66	A	10.1	A	8.8	A
40	5	0.71	a	0.66	a	11.4	a	9.0	a
	10	0.79	b	0.61	a	11.7	a,b	9.2	a
	18	0.79	b	0.50	b	13.0	b	9.1	a
	26	0.68	a	0.46	b	13.8	b	9.4	a
Average		0.74	B	0.56	B	12.5	B	9.2	A
60	5	0.66	a	0.55	a	14.2	a	9.7	a
	10	0.74	b	0.51	a	15.3	b	10.0	a
	18	0.77	b	0.52	a	15.9	b	9.8	a
	26	0.61	a	0.42	b	16.7	c	9.7	a
Average		0.69	B	0.50	B	15.5	C	9.8	A
ANSI Standard, MDF		0.60		- - -		- - -		10.0	

[1] Means in columns with common letters were not significantly different at the 5% level within the type of soy component. Significance for degree of hydrolysis is indicated within each replacement level seperately.

[2] American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

CHAPTER 4

Effects of degree of hydrolysis on soy flour and polyamide-epichlorohydrin bond strength and stability

A paper to be submitted to *The Journal of the American Oil Chemists Society*

J.F. Schmitz and D.J. Myers

Abstract

This study examined the effects of protein hydrolysis on the performance of soy flour (SF) in polyamide-epichlorohydrin (PAE) resin blends for use as wood adhesives. Resins were applied in a two ply wood system over a 30 day trial period and examined for shear strength in dry, soaked, and boiled conditions. Blends with PAE having high reactivity with carboxyl and hydroxyl groups led to increased viscosity over the test period, but no difference in the shear strength was observed over the 30-day period. Degree of protein hydrolysis (DH) significantly affected shear strength, with 10% DH being the maximum before both wet and dry strength decreased.

Key words: soy flour, soy hydrolysates, soy adhesives, protein adhesives, enzyme processing

Introduction

In 2008 the estimated need for wood adhesives in North America was over 1.6B kg (1). In recent years many concerns have been raised about diminishing

petroleum resources and health issues stemming from the manufacture and use of petroleum based adhesives. Likewise there has been increased consumer interest for biobased products. Research surrounding biobased adhesives has been widespread covering potential markets such as wood products, packaging, and consumer adhesives (2-6), and has utilized biorenewable chemicals such as proteins, tannins, glycerol, and lignin (7-9).

In a recent adhesives market summary, Orr (10) estimated the total market potential for soy based adhesives to be as large as 430M kg per year. Soy protein adhesives were first developed in the 1920s and plywood usage peaked at nearly 45M kg in 1956 (11). Recent research has once again focused on plywood resins (4, 12), but also expanded to include the wide variety of wood products that are available in today's market. In the honeymoon system for finger-jointed lumber, Steele *et al*. (13) demonstrated soy protein isolate (SPI) was highly reactive with phenol-resorcinol-formaldehyde, but the two components needed to be separated until application due to high reactivity and a short potlife when mixed prior to application. Soy flour/phenol formaldehyde resins containing up to 70% soy flour were developed for oriented strandboard and plywood (2, 14). Additional studies have examined the adhesive nature of SPI denatured with various chemicals, but have continued to report water resistance as a weakness of these adhesives (15-18).

Li *et al*. (19) first examined soy protein combined with Kymene®, a commercial polyamide-epichlorohydrin (PAE) used in the paper industry to increase wet strength. Kymene® was proposed as a crosslinking agent with SPI when SPI-

Kymene® was found to have comparable shear strength to PF resin. Follow up studies have shown enhanced durability of SPI/PAE at the SPI isoelectric point (20). In both applications the resin system was a highly viscous material with short potlife, and it was only suitable for rollcoat applications.

Unlike alkaline hydrolysis the use of enzymes with soy flour (SF) can tailor protein hydrolysate products with different viscosities and strength attributes in a PF system. In this study SF was modified with enzymes and crosslinked with two PAEs of differing functional reactivities. It is hypothesized that soy hydrolysates paired with PAE have suitable strength attributes and could create adhesives with lower viscosity, making then suitable for broader use in the wood products industry.

Experimental Procedures

Materials. HoneySoy90, a defatted soybean flour with 53.0% protein, 1.2% residual fat, and a specified PDI of 90, was procured from Cenex Harvest States in Mankato, MN). Soy flour dispersions with 25% solids were adjusted to pH 8.0 with 1.0 N sodium hydroxide. Dispersions were stirred at 150 rpm, and brought to 50°C in a water bath. After 20 min at constant temperature, the dispersions were treated with a 0.10% (w:v) dosage of Protex 89L (Genencor Intl.). Protex 89L is a bacterial serine endopeptidase derived from a genetically modified strain of *Bacillus subtilis*. DH was measured by using the OPA method as described by Nielsen *et al*. (21). Hydrolysis of the protein dispersions was stopped at 5, 10, 15, and 20% DH. Hydrolysis was halted by inactivating the enzyme by heating the material at 80°C for 5 min. Hydrolysis of the carbohydrate fraction of soy flour was performed with a

0.2% (w/v) dose of Multifect CX GC for 8 h. Multifect CX GC is a cellulase derived from *Trichoderma reesei*.

Two commercially available PAEs were obtained from Hercules Inc. (Wilmington, DE): POLYCUP® 172 (P172) and ChemVisions™ CA1000 (CV1000). Both are thermosetting crosslinkers reactive with amine, carboxyl, hydroxyl, and thiol functional groups. The initial viscosities of P172 and CV1000 were 50 and 120 cps at 23°C respectively.

Preparation of SF-PAE Adhesives. SF hydrolysates and PAE crosslinker were blended in ratios of 8:1, 9:1, and 10:1 in all combinations. Resin blends were adjusted to pH 8.0 using 1.0 N sodium hydroxide, and then mixed for 60 min at 40°C. Viscosity measurements were taken once the resin blends cooled to room temperature and again after 3, 10, 20, and 30 days using a LabLine 4559 viscometer from Lab-Line Instruments, Inc (Melrose Park, IL) and a $^{\#}4$ probe at 50 rpm. A slow rotational speed was used to minimize the shear-thinning effect of the resin blends on viscosity measurements.

Preparation and Evaluation of Lap Shear Wood Composites. Maple veneer was a gift from Bacon Veneer in Grundy Center, IA. Sample plys were cut to 18 cm x 5 cm with the grain running parallel to the short dimension. Adhesive was applied at the rate of 0.20 g/cm^2 on a dry adhesive basis. Resin load was determined such that adhesive failure was prevalent in shear strength determination, and >20% wood failure occurred in <10% of the samples. A second ply was stacked over the

adhesive and hot-pressed at 145°C for 2.0 min at 1.4 MPa on a 2.5 MPa hydraulic press from Wabash MPI (Wabash, IN). Post curing of lap shear samples was done at ambient conditions in stacks of 20 samples wrapped in muslin bags for 24 hours. Lap shear samples were made on days 1, 10, and 20 days after resin preparation. Samples were cut to a width of 2.5 cm and shear strength was tested on an MTI Phoenix Ultimate Testing Machine from Measurements Technology, Inc. (Roswell, GA) according to American Society for Testing and Materials (ASTM) standard method D-906 (22). The bonding area of testing specimens was 6.3 cm^2. (2.5 cm x 2.5 cm). Figure 1 depicts the final specimen dimensions. The crosshead speed during shear strength determination was 1.0 mm/min. Bond strength was reported as the maximum shear strength in MPa at breakage between two pieces of veneer.

Wood Composite Wet Strength. A water soaking and drying (WSAD) test was performed to evaluate water resistance for interior applications as described in previous works (16, 17). Bonded wood composites were soaked in water at ambient lab conditions for 24 h, dried at room temperature in a fume hood for 24 h, and the lap shear strength was measured. An additional boiling water test (BWT) was performed where test specimens were boiled in water for 4 h and then dried for 20 h at 65°C. Specimens were boiled in water again for 4 h and cooled with tap water. Specimens were tested wet for shear strength (BWT-W) as well as some specimens were air dried in a fume hood for 24 h (BWT-D).

Experimental Design. Three replicates of the experiment were performed with unique batches of SF hydrolysates for each replicate. Lap shear composites were created such that 20 sample specimens were available for each shear strength measurement. Results were analyzed using ANOVA with the general linear model in Statistical Analysis Software Program version 9.1 (SAS Institute, Inc., Cary, NC). Significant effects are reported based on $p<0.05$.

Results and Discussion

P172 and CV1000 are both aqueous cationic PAE resins used commercially in the paper industry. The general chemistry of PAE resins is well documented and describes the four-membered ring structure, the hydroxyl-azetidium, as the key functional group in PAE crosslinking and strength development (23-26). Combining the known reactions of PAE resins and the common structures of SF, the reactions proposed among the two include: 1) PAE homo-crosslinking, 2) the azetidium group reacting with amine, carboxylic, and hydroxyl side chains, 3) the azetidium group reacting with either the amino or carboxy terminal ends of peptides, and 4) the azetidium group reacting with hydroxyl groups of carbohydrates (Figure 2).

The resin viscosity was observed for 30 days after blending the resin similar to shear strength testing. Figure 3 shows the viscosity profile for the resin blends at 5,10, 15, and 20% DH. There were no appreciable differences among viscosity trends relative to DH, but the two PAEs behaved differently in resin blends. SF adhesive blends with P172 would have limited application techniques beyond roll-

coating due to the increasing viscosity over the 30 day period. P172 was chosen as one of the crosslinking PAEs because its specification indicated increased reactivity with both hydroxyl and carboxyl groups that are prevalent in soy flour and wood lignocellulose. The viscosity profiles seem to support the manufacturers claim. After 30 days, viscosity of the CV1000 blends had not increased drastically, and show they are not only stable, but could be suitable for multiple adhesive application techniques such as spraying or roll coating.

When it comes to dry strength measurements, there was no evidence of increased tensile strength though. Figure 4 shows the dry strength was consistent over the testing period, but decreased as DH increased. Increased reactivity in P172 was observed in viscosity, but after curing, both PAE crosslinkers performed equally well in shear strength.

Table 1 reports the mean tensile strength values across the entire testing period. Both DH and SF:PAE ratio were significant factors affecting the performance of SF/PAE resins. Shear strength for the 10:1 SF/PAE ratio was significantly lower than for the 8:1 and 9:1 ratios, and there was no delamination of the glue-line for any of the dry strength or soaked water specimens. Similar to higher soy content in the resin blend though, increased hydrolysis of the soy flour also decreased shear strength of the glue line. Comparable trends, yet statistically lower shear strengths were recorded after the WSAD procedure relative to the dry shear strength. Overall, there was an approximately 20% decrease in WSAD shear strength for the 8:1 and 9:1 SF/PAE ratios from the dry shear strength. The 10:1 ratio reduced shear strength by approximately 26%.

The shear strength results are more drastic when BWT is considered. No glue-line delamination was observed outside of the BWT procedure. At all 10:1 SF/PAE ratios, the glue-lines failed during the first or second boiling step. Dried BWT specimen maintained measureable strength at all DH values for the 8:1 and 9:1 SF:PAE ratios. Dry shear strengths of the 8:1 and 9:1 SF:PAE ratios were not significantly different from one another nor were the WSAD results after two boiling cycles. In both the 8:1 and 9:1 SF/PAE blends, 10 and 15% DH were similar, but 5% DH had decreased dry and wet shear strength. Shear strength in blends with 20% DH SF was also significantly lower than the shear strength at 10 and 15% DH. Results conclude that longer peptides do not crosslink and cure with PAE as effectively as shortened peptides. However, hydrolysis beyond 15% resulted in decreased shear strengths.

There was no significant difference between wet BWT samples prepared with SF at 5 or 10% DH. The 8:1 and 9:1 SF/PAE ratios did not delaminate during boiling, but when DH was >10% there was no measureable shear strength when they were wet. The glue-line simply gave out when tensile force was applied. Overall, there was nearly a 50% reduction in strength between the dry shear strength and the BWT specimen when tested wet.

Conclusions

The present work demonstrated the crosslinking ability of commercial paper-sizing agents with SF and determined the effects of protein hydrolysis on shear strength. Shear strength was dependent on extent of protein hydrolysis and ratio of

SF to crosslinker, but no interaction was found between the two factors. Enzyme hydrolysis is an effective means to reduce resin viscosity and careful selection of PAE functionality can result in resins with extended potlife and potential use in multiple resin application systems. Finally, the statistical significance of DH verifies the longstanding belief that enzyme processing is a suitable means to tailor protein fractions for varying applications such as different crosslinkers.

Acknowledgements

This work was supported by the USDA, CSREES grant 2008-34432-10325, and was performed in cooperation with Genencor International (Rochester, NY). The authors express gratitude to Hercules, Inc (Wilmington, DE) for the polyamide precursors and Bacon Veneer (Grundy Center, IA) for the maple veneer.

References

(1) Omni Tech International, LTD. Wood adhesives: A market opportunity study. httpwww.unitedsoybean.orgUploadedFilesLibrarypdf_25241M%20Adhesive.pdf. (Accessed June 2009).

(2) Kuo, M.L., Adams, D., Myers, D.J., Curry, D., Heemstra, H., Smith, J.L., Bian, Y., 1998. Properties of wood/agricultural fiberboard bonded with soybean-based adhesives. For. Prod. J. 48, 71-75.

(3) Wescott, J.M., Frihart, C.R., 2004. Competitive soybean flour/phenol formaldehyde adhesive for oriented strandboard. 38th International Wood Composite Symposium, Pulman, WA.

(4) Hojilla-Evangelista, M.P., Dunn Jr, L.B., 2001. Foaming properties of soybean protein-based plywood adhesives. J. Am. Oil Chem. Soc. 78, 567-572.

(5) Choi, W.Y., Lee, C.M., Park, H.J., 2006. Development of biodegradeable hot-melt adhesive based on poly-ε-caprolactone and soy protein isolate for food packaging system. Lebensm-Wiss. Technol. 39, 591-597.

(6) Zhong, Z., Sun, X.S., 2001. Properties of soy protein isolate/polycaprolactone blends compatalized by methylene diphenyl diisocyanate. Polymer. 42, 6961-6969.

(7) Pizzi, A., 2006. Recent developments in eco-efficient biobased adhesives for wood bonding: Opportunities and issues. J. Adhes. Sci. Technol. 20, 829-846.

(8) Lorenz, C.D., Stevens, M.J., Wool, R.P., 2004. Fracture behavior of Triglyceride-based adhesives. J. Polym. Sci. Pol. Phys. 42, 3333-3343.

(9) Kazayawoko, J.S.M., Reidl, B., Poliquin, J., Barry, A.O., Matuana, L.M., 1992. A lignin-phenol formaldehyde binder for particleboard. Holzforschung. 46, 257-262.

(10) United Soybean Board. Soy based wood adhesives. http://www.unitedsoybean.org/UploadedFiles/Library/pdf_25241M%20Adhesive.pdf. (Accessed June 2009).

(11) Lambuth, A.L., 1977. Soybean glues. In “Handbook of Adhesives,” I. Skeist ed. Van Nostrand Reinhold Co., New York, NY.

(12) Hojilla-Evangelista, M.P., 2002. Adhesive qualities of soybean protein-based foamed plywood glues. J. Am. Oil Chem. Soc. 79, 1145-1149.

(13) Steele, P.H., Kreibich R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy based adhesives. Adhes. Age. 41, 49–56.

(14) Yang, I., Kuo, M.L., Myers, D.J., 2006. Bond quality of soy based phenolic adhesives in southern pine plywood. J. Am. Oil Chem. Soc. 83, 231-237.

(15) Zhong, Z.K., Sun, X.S., Wang, D.H., 2003. Wet strength and water resistance of modified soy protein adhesives and effects of drying treatment. J. Polym. Environ. 11, 137-144.

(16) Sun, X.S., Bian, K., 1999. Shear strength and water resistance of modified soy protein adhesives. J. Am. Oil Chem. Soc. 76, 977-980.

(17) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. *Ibid*. 77, 705-708.

(18) Zhong, Z.K., Sun, X.S., Fang X.H., Ratto, J.A., 2002. Adhesive strength of guanidine hydrochloride – modified soy protein for fiberboard application. Int. J. Adhes. Adhes. 22, 267-272.

(19) Li, K., Peshkova, S., Geng, X., 2004. Investigation of soy protein-Kymene® adhesive systems for wood composites. J. Am. Oil Chem. Soc. 81, 487-491.

(20) Zhong, Z., Sun, X.S., Wang, D., 2007. Isoelectric pH of polyamide-epichlorohydrin modified soy protein improved water resistance and adhesion properties. J. Appl. Polym. Sci. 103, 2261-2270.

(21) Nielsen, P.M., Petersen, D, Dambmann, C., 2001. Improved method for determining food protein degree of hydrolysis. J. Food Sci. 66, 642-646.

(22) American Society of Testing and Materials, 1999. Standard Test method for evaluating wood-base lap shear strength. Designation: D906-99. West Conshohocken, PA, pp. 243-246.

(23) Keim, G.I., 1960. Cationic thermosetting polyamide-epichlorohydrin resins for preparing wet-strength adhesive. U.S. Patent 2,926,154.

(24) Keim, G.I., 1960. High wet-strength paper. U.S. Patent 1,929,116.

(25) Espy, H.H., Rave, T.W., 1988. The mechanism of wet strength development by alkaline-curing polymer-epichlorohydrin resins. TAPPI J. 71, 133-137.

(26) Espy, H.H., 1995. The mechanism of wet-strength development in paper: a review. *Ibid.* 78, 90-99.

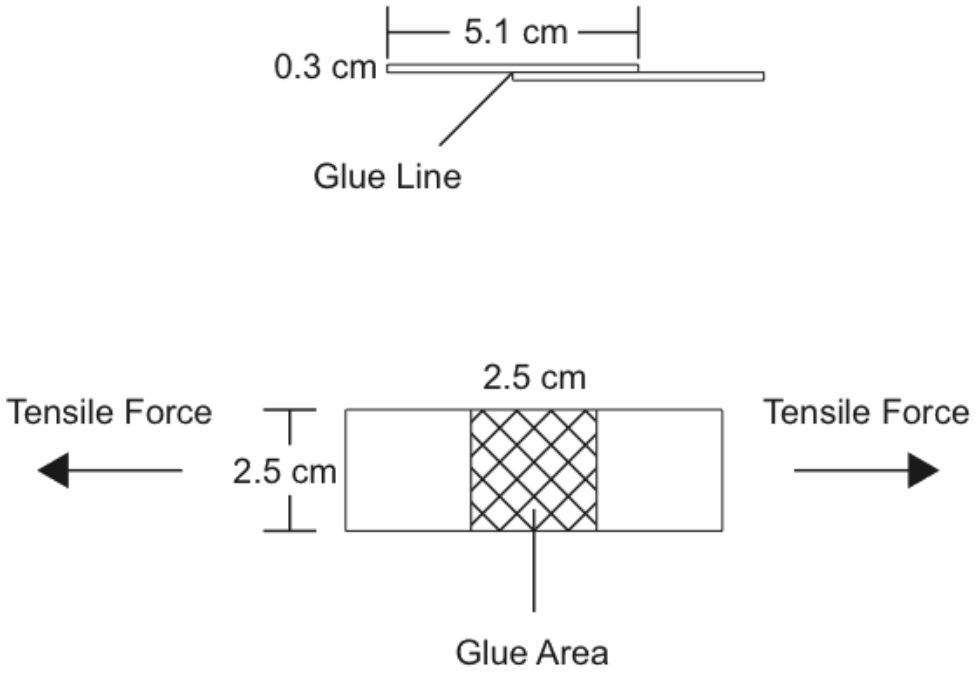

Figure 4-1. Lap shear dimensional diagram

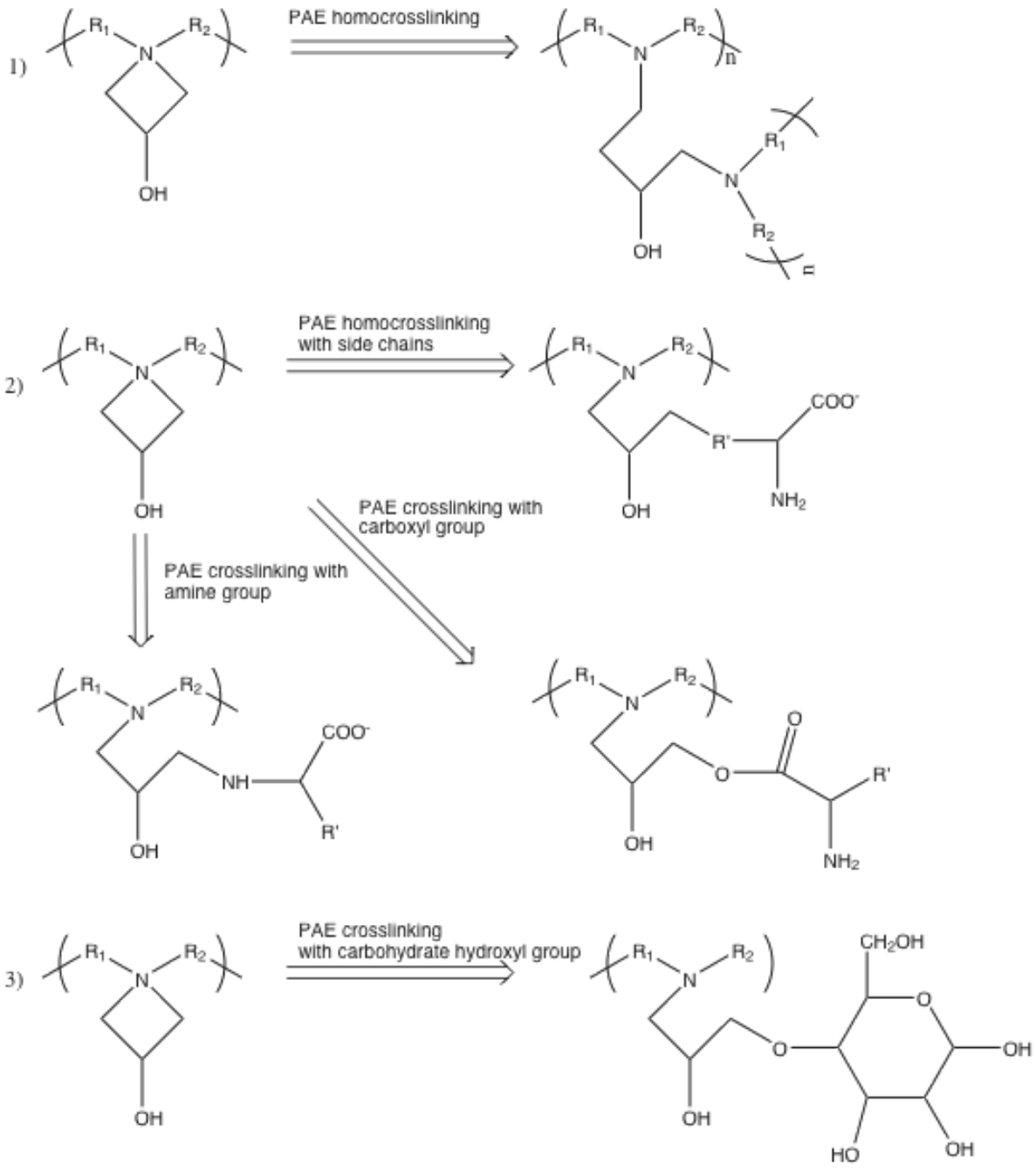

Figure 4-2. Potential PAE reactions with itself and soy flour components

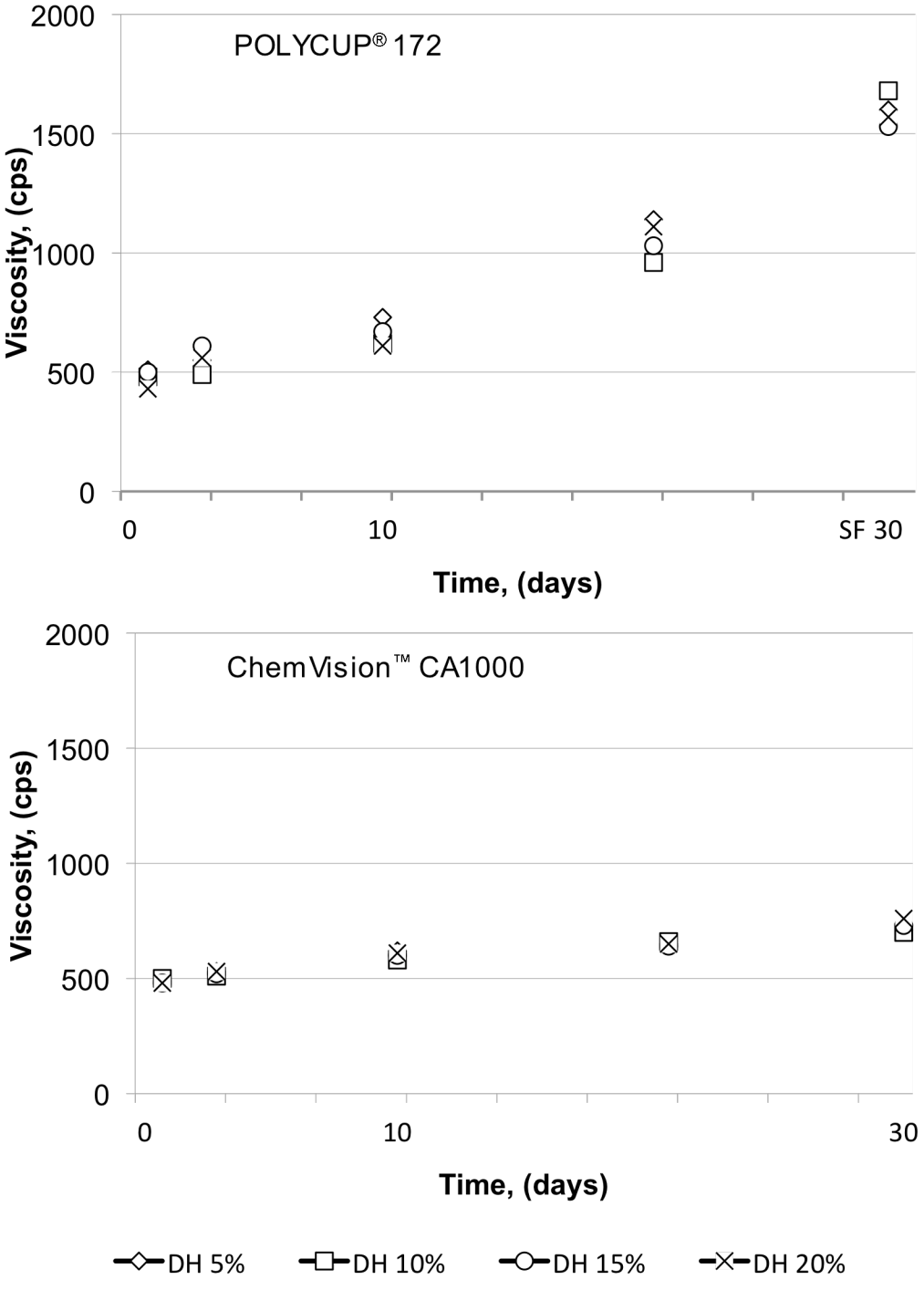

Figure 4-3. Viscosity of SF/PAE resin blends over 30 day period

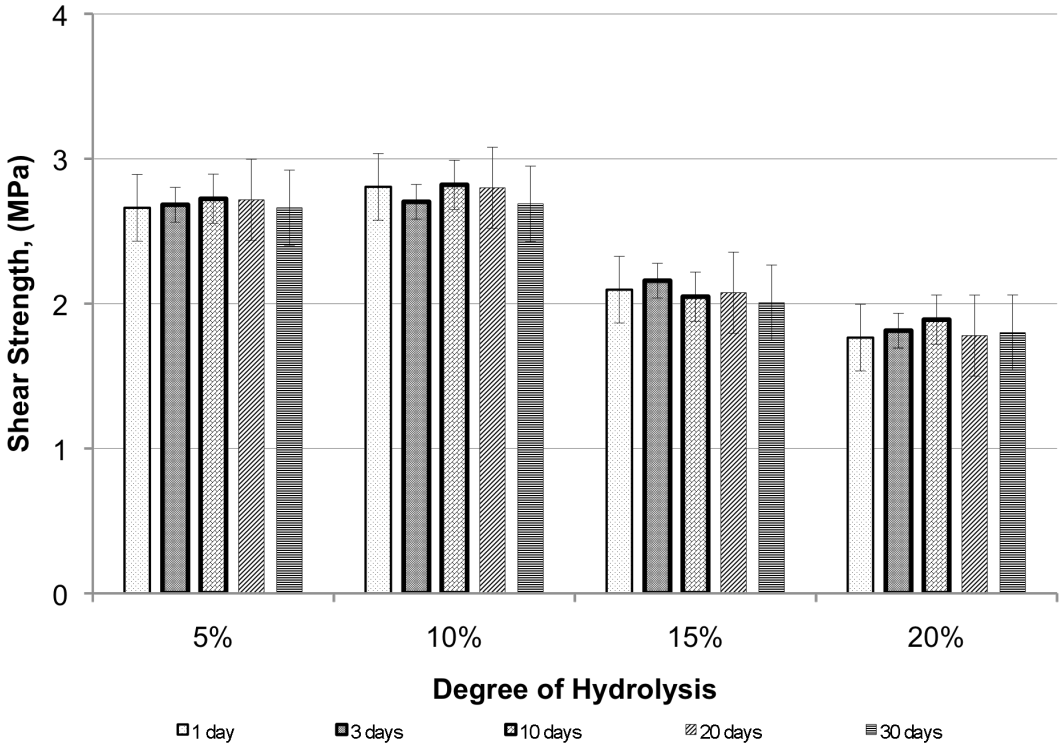

Figure 4-4. Dry shear strength of 9:1 soy/PAE resin blends over 30 day period

Error bars indicate 95% confidence interval.

Table 4-1. Dry and wet shear strength of soy hydrolysate/PAE resin blends

Resin Properties			Shear Strength (MPa)							
DH (%)	Soy/PAE ratio	PAE	Dry [1]		WSAD [2]		BWT [3] - D		BWT [3] - W	
5% [*]	8:1[**]	P172	2.62		2.16		2.08		1.41	
		CV1000	2.72		2.20		2.17		1.52	
		Average	2.67	a	2.18	a	2.13	a	1.46	a
	9:1	P172	2.70		2.12		2.03		1.45	
		CV1000	2.68		2.21		2.18		1.41	
		Average	2.69	a	2.16	a	2.10	a	1.43	a
	10:1	P172	2.48		1.83		DL		DL	
		CV1000	2.46		1.92		DL		DL	
		Average	2.47	b	1.87	b	DL		*DL*	
10%	8:1	P172	2.71		2.22		2.05		1.34	
		CV1000	2.66		2.14		2.13		1.43	
		Average	2.69	a	2.18	a	2.09	a	1.39	a
	9:1	P172	2.79		2.16		2.10		1.48	
		CV1000	2.74		2.19		2.14		1.39	
		Average	2.76	a	2.18	a	2.12	a	1.43	a
	10:1	P172	2.34		1.96		DL		DL	
		CV1000	2.43		1.85		DL		DL	
		Average	2.39	b	1.91	b	DL		*DL*	
15%	8:1	P172	2.14		1.90		1.52		DL	
		CV1000	2.18		1.85		1.63		DL	
		Average	2.16	a	1.88	a	1.57	a	*DL*	
	9:1	P172	2.10		1.92		1.59		DL	
		CV1000	2.05		1.82		1.61		DL	
		Average	2.08	a	1.87	a	1.60	a	*DL*	
	10:1	P172	1.92		1.65		DL		DL	
		CV1000	1.84		1.52		DL		DL	
		Average	1.88	b	1.59	b	*DL*		*DL*	
20%	8:1	P172	2.14		1.81		1.43		DL	
		CV1000	2.10		1.73		1.47		DL	
		Average	2.12	a	1.77	a	1.45	a	*DL*	
	9:1	P172	2.10		1.77		1.48		DL	
		CV1000	2.00		1.80		1.43		DL	
		Average	2.05	a	1.79	a	1.45	a	*DL*	
	10:1	P172	1.78		1.56		DL		DL	
		CV1000	1.71		1.42		DL		DL	
		Average	1.75	b	1.49	b	DL		DL	

[1] Dry strength is measure of shear strength of cured lap shear specimens

[2] WSAD is measure of shear strength following specimens soaking 20 h in 23°C distilled water

[3] BWT is shear strength following two cycles of 4 h boiling water, measured both dry and wet

[4] Column means with common letters were not significantly different at the $p < 0.05$ level within each DH level

[*] Statistical analysis showed that degree of hydrolysis was significant at $p > 0.05$

[**] Statistical analysis determined the ratio of PAE in the resin had a significant effect on strength at $p > 0.05$

CHAPTER 5

Urea enhanced soy flour/polyamide-epichlorohydrin adhesives

A paper to be submitted to *The Journal of the American Oil Chemists Society*

J.F. Schmitz and D.J. Myers

Abstract

Crosslinked soy flour (SF) systems have been considered in numerous applications as alternatives to petroleum derived adhesives. Soy protein isolate (SPI) alone results in considerable dry strength, but wet strength and water resistance do not meet the needs of commercial wood products. SF crosslinked with polyamide-epichlorohydrin (PAE) was tested against SPI and with or without urea. Glue strength, water resistance, and static bending properties were examined using ASTM standards. Dry testing indicated no appreciable difference with urea added to the resin forumulation. Wet shear strength and water resistance in medium density fiberboard specimens (MDF) showed that SF mixed with urea prior to adding PAE enhanced wet properties of plywood and MDF specimens. The shear strength of SF-urea/PAE formulations was similar to the strength of SPI/PAE and SPI-urea/PAE supporting the hypothesis that urea is capable of incorporating the carbohydrate fraction of SF into the overall adhesive matrix.

Key words: soy flour, soy hydrolysates, soy adhesives, protein adhesives, enzyme processing

Introduction

In the early 20th century when manufactured wood products were beginning to expand in market share, soy adhesives were the prevalent plywood adhesive. The technologies described in the patents of Laucks and Davidson, and Johnson (1, 2) changed very little before synthetic and petroleum based adhesives took over as the mainstays in adhesive formulations (3, 4). Consumer interest in biobased and green products has opened a new avenue for soy based adhesives to regain prominence in manufactured wood products. Interest has grown due to concerns about declining petroleum resources and health issues stemming from manufacturing and using petroleum based adhesives. Research has extended across all manufactured wood products, such as plywood, oriented strandboard, fiberboard, finger-jointed lumber, and lower grade adhesives for packaging (5-14).

An emerging interest in biobased adhesives has been the formulation of formaldehyde free resins. Polyamide-epichlorohydrin (PAE) has a longstanding tradition in the paper industry for contributing to wet strength, but recently has been identified as a potential crosslinker for protein-based wood adhesives as well. Li *et al*. (15) first proposed Kymene®, a commercial PAE, as a crosslinker by demonstrating the dry and wet strength of SPI/Kymene® blends. Additional work has suggested optimal conditions for wet strength in soy/Kymene® resins is at the protein isoelectric point (16), and that enzyme controlled hydrolysis can produce SF/PAE blends to formulate resins with extended potlife (Chapter 4).

Wet strength continues to be an area of concern and greatest interest for formaldehyde-free resins. The major drawback of denatured SPI as a sole

adhesive is the resulting water resistance (7-9). Amino acid side chain modifications have been explored to increase water resistance of soy protein adhesives. Liu and Li (17) reported that derivatives from mussel proteins could be reacted with SPI to enhance wet strength and durability, and in 2007 they reported crosslinking SPI with maleic anhydride and poly(ethylimine) exhibits greater water resistance than SPI alone (18). Sun and Bian (7) showed that treating SPI with urea led to increased water resistance in a pure soy adhesive system and they presumed that hydrogen bonding enhanced the adhesive matrix and decreased water resistance. Carbohydrate based research has shown urea to be an effective crosslinking agent in different chemical systems. Hydroxyalkyl urea is desired in abrasive adhesives for reactivity with both hydroxyl and amine groups (19). Ohlan *et al*. (20) demonstrated the ability of urea to complex with a variety of organic molecules included starches, leading to stable aqueous solutions.

Previous work has established the limits of protein hydrolysis for SF/PAE resins and identified that increased hydroxyl reactivity in the PAE leads to reduced potlife (Chapter 4). The present work outlines a simple, yet effective, chemical additive to the SF hydrolysate to enhance the durability properties of SF/PAE adhesives. Urea is believed to hydrogen bond with both the carbohydrate and protein components of SF hydrolysates without affecting the reactivity with PAE during curing. The result is stable solutions in the presence of PAE crosslinkers and increased water resistance in the cured wood product.

Experimental Procedures

Preparation of Adhesives. HoneySoy90, a defatted soybean flour, was procured from Cenex Harvest States in Mankato, MN. The specified PDI of HoneySoy90 was 90, and protein and residual fat were measured as 53.0% and 1.2% respectively. Using HoneySoy90, SPI was made according to the lab-scale procedure given by Deak and Johnson (21). Dispersions of both SF and SPI with 25% solids were adjusted to pH 8.0 with 1.0 N sodium hydroxide. Dispersions were stirred at 150 rpm and brought to 50°C in a water bath. After 20 min at constant temperature, the dispersions were treated with a 0.25% (w:v) dosage of Protex 89L at 50°C. The degree of hydrolysis (DH) was measured by the OPA method as described by Nielsen *et al*. (22). Hydrolysis of the dispersions was stopped at 10% DH. Hydrolysis of the carbohydrate fraction of SF was performed with a 0.2% (w/v) dose of Multifect CX GC (Genencor, Intl, Rochester, NY) for 8 h. Multifect CX GC is a cellulase derived from *Trichoderma reesei*.

To test the theory that urea enhances crosslinking, 10% dry weight of soy solids was added as urea to both SF hydrolysate and SPI hydrolysate. The mixtures of hydrolysate and urea were mixed at 40°C for 1 h. ChemVisions™ CA1000 (PAE) was acquired from Hercules Inc. (Wilmington, DE), and blended with the soy-urea mixture at a ratio of 1:9 by weight of hydrolysate solids. Viscosity was monitored every three days for 30 days using a LabLine 4559 viscometer from Lab-Line Instruments, Inc. (Melrose Park, IL) and a $^{\#}4$ probe at 50 rpm. A slow rotational speed was used to minimize the shear-thinning effect of the resin blends.

Preparation and Evaluation of Lap Shear Wood Composites. Maple veneer was a gift from Bacon Veneer (Grundy Center, IA). Sample plys were cut to 18 cm x 5 cm with the grain running parallel to the short dimension. The bonding area was 6.3 cm^2 (2.5 cm x 2.5 cm). Adhesive was applied at the rate of 0.20 g/cm^2 on a dry adhesive basis. Resin load was determined such that adhesive failure was prevalent in shear strength determination, and >20% wood failure occurred in <10% of the samples. A second ply was stacked over the adhesive and hot-pressed at 145°C for 2 min at 1.4 MPa on a 2.5 MPa hydraulic press from Wabash MPI (Wabash, IN). Post curing of lap shear samples was done at ambient conditions in stacks of 20 samples wrapped in muslin bags for 24 h. Samples were cut to a width of 2.5 cm prior to testing on an MTI Phoenix Ultimate Testing Machine from Measurements Technology, Inc. (Roswell, GA). Figure 1 depicts the final specimen dimensions. The crosshead speed during shear strength testing was 1 mm/min. Bond strength was reported as the maximum shear strength at breakage between two pieces of maple veneer. Lap shear specimens were made for each adhesive blend after 1, 10, 20, and 30 days of storage.

Wood Composite Wet Strength. A water soaking and drying (WSAD) test was performed to evaluate water resistance for interior applications as described in previous work (7, 8). Bonded wood composites were soaked in water at ambient lab conditions for 24 h, dried at room temperature in a fume hood for 24 h, and the lap shear strength was measured. An additional boiling water test (BWT) was performed where test specimens were boiled in water for 4 h and then dried for 20

h at 65°C. Specimens were boiled in water again for 4 h and cooled with tap water. Specimens were tested wet for shear strength (BWT-W) as well as some specimens being air-dried in a fume hood for 24 h (BWT-D).

Fiberboard Fabrication and Evaluation. MDF was prepared with pinewood fiber procured from Jeld-Wen, Inc. (Dubuque, IA). Prior to use, pinewood fiber was oven dried at 180°C to about 2% moisture. For each sample replicate enough fiber to make two 41 cm x 41 cm x 1.3 cm MDF boards at a target density of 0.80 g/cm^3 was placed into a tumbler. Adhesive blends were atomized and sprayed onto the fiber at 8% application rate based on dry fiber weight. Following the completion of adhesive spraying plus 2 min additional tumbling, fiber was removed from the tumbler with the aid of a vacuum/blower. Fiber was hand-laid into a 41 cm x 41 cm forming box and prepressed. Boards were pressed with a 16 MPa hydraulic press from Wabash MPI (Wabash, IN) with sufficient pressure to allow closing within 15 sec. All boards were pressed with an eight minute press cycle at 200°C and 5.3 MPa. Post curing of fiberboards was done at ambient conditions in stacks of 10 fiberboards wrapped in muslin bags for 36 h.

Fiberboards were trimmed to 35.6 cm x 35.6 cm specimens and prepared for static bending (modulus of elasticity [MOE] and modulus of rupture [MOR]) and strength perpendicular to surface (internal bond testing [IB]) in accordance to ASTM Standard D1037-99 (23). All mechanical strength attributes were measured on an MTI Phoenix Ultimate Testing Machine from Measurements Technology, Inc. (Roswell, GA). Static bending was performed on a 3-point bending setup with a 30

cm base. Dimensional stability samples of 7.6 cm x 10.2 cm were obtained from bending test specimens after failure. Dimensional stability samples were conditioned at 65% relative humidity and 23°C for five days prior to testing. Dimensional stability tests were measured as percentage thickness swell after 2 h of boiling (TS-2B) and 24 h of soaking (TS-24B) in distilled water. Following the 2 h boil measurements, samples were dried and residual IB specimens were obtained (IB-B). For MOR and MOE there were two samples per board and 8 IB samples per board. Figure 1 depicts the scheme used for cutting samples from the trimmed fiberboard.

Experimental Design. Three replicates of the experiment were performed with unique batches of SF hydrolysates for each replicate. Lap shear composites were produced such that 20 sample specimens were available for each shear strength measurement. MDF boards were made in duplicate for each treatment in each hydrolysates replicate. Results were analyzed using ANOVA with the general linear model in Statistical Analysis Software Program version 9.1 (SAS Institute, Inc., Cary, NC). Pairwise comparisons were made and significant effects are reported based on $p<0.05$ with the Bonferroni adjustment.

Results and Discussion

The published reactions of PAE (24, 25) include a variety of chemical reactions that may occur in SF/PAE blends. Chief among them are homocrosslinking with itself, and reaction of the azetidium group with carboxyl,

amine, and amino acid side chain groups. Likewise, the azetidium group may crosslink with hydroxyl groups in the carbohydrate fraction. Extensive crosslinking leads to a stable and well defined three dimensional network. Numerous soy adhesive studies have previously demonstrated a drawback to SF utilization is decreased wet strength and durability. Urea has similar functionality to the crosslinking groups mentioned above. With two amine groups and a double bonded oxygen, urea may improve wet strength and durability of the cured PAE network (20).

As described in the previous chapter, there was no significant change in dry or WSAD shear strength over time. The adhesive potential remained the same for each resin blend during extended resin storage. There were significant changes in the resin blends themselves over the course of time though. Unblended SF and SPI hydrolysates were unstable at ambient storage conditions as evidenced by increased viscosity within six days and visible mold and bacteria growth within ten days. Hydrolysates with urea, PAE, or urea and PAE maintained stable viscosities and did not exhibit any visible signs of microbial degradation.

Table 1 reports the mean results for lap shear test results. SPI and SF hydrolysates alone resulted in the lowest dry shear strength, and were significantly different from all resin blends containing either PAE or urea. PAE blended with urea had an intermediate dry strength, whereas all resin blends with soy hydrolysates, urea, and PAE had the highest shear strength. Lap shear specimens made with pure soy hydrolysate delaminated in all cases during soaking and boiling tests. There were no significant differences between WSAD prepared from SPI or

SF with or without urea when blended with PAE. The more strenuous boiling test revealed differences between blends with and without urea. In BWT tests, all samples without PAE delaminated during the preparation procedure. Specimens prepared with SPI did not exhibit any significant difference in shear strength. SF with urea and PAE showed similar dry and wet strengths after boiling to the SPI specimens, but SF specimens prepared without urea resulted in lower shear strength. Lap shear results show few differences, but strenuous test procedures indicate urea reacts with SF hydrolysates and PAE, thereby increasing wet shear strength in PAE resin blends.

There were few significant differences in mechanical properties of MDF. The results in Table 2 show results of static bending and internal bond testing. By virtue of making MDF, the results indicate that formulations of soy hydrolysate blended with PAE and or urea have a low enough viscosity to work in atomized air applications. Additionally IB results reinforce that PAE enhances adhesive strength of SF or SPI alone. Similar to the BWT lap shear results, the IB of SF/PAE resin was statistically different than that of SPI/PAE with and without urea. SF with urea and PAE increased the SF IB value to a comparable level with SPI blended with PAE. Table 3 reports the MDF results that best reinforce the hypothesis that urea is capable of crosslinking SF components to form an enhanced adhesive matrix. Increased thickness swell in SF/PAE compared to SPI/PAE indicated dimensional stability decreased with the use of SF hydrolysates in resin formulation. However incorporation of urea with SF stabilized thickness swell and resulted in thickness swell values similar to SPI both with and without urea. Lower thickness swell

values were observed for the 24-h soak test compared to the 2-h boil, but the significance between treatments was the same for both tests though.

Not all of the resin treatments met the minimum standard for interior grade MDF defined by the American National Standards Institute (ANSI). Tables 2 and 3 the report the minimum requirements for comparison sake. All resin treatments exceeded the MOE and MOR standard of $2.4x10^3$ 24.0 MPa respectively. Despite not being significantly different from one another, SF-Urea alone did not exceed the minimum IB standard of 0.60 MPa, whereas SPI-Urea did. Thickness swell for SPI with urea and with urea/PAE both met the ANSI maximum value of 10% swell. For SF blends however, only the SF-urea/PAE resin met the ANSI standard.

Conclusions

Results continue to support previous findings that PAE is capable of crosslinking SPI and SF for use in wood adhesives. When compared by themselves SPI and SF blended with PAE are significantly different from one another in a multitude of strength tests including shear strength, internal bond, and dimensional stability. SF blended with PAE alone exhibited significantly lower strength than SPI with PAE. Presumably the carbohydrate fraction in SF is less reactive with PAE and decreases both dry and wet shear strength and water durability. Urea added to SPI/PAE had no significant effect. SF mixed with urea significantly improved adhesive characteristics in shear strength and MDF properties, indicating that urea reacts with the carbohydrate fraction in SF and the PAE polymer structure to enhance adhesive properties.

Acknowledgements

This work was supported by the USDA, CSREES grant 2008-34432-10325, and was performed in cooperation with Genencor International (Rochester, NY). The authors are grateful to Hercules, Inc. (Wilmington, DE) for the PAE resin, Bacon Veneer (Grundy Center, IA) for the maple veneer, and Jeld-Wen Inc. (Dubuque, IA) for the wood fiber.

References

(1) Laucks, I.F., Davidson, G., 1928. Vegetable glue and making of the same. U.S. Patent 1,691,661.

(2) Johnson, 0., 1928. Process of treating soya beans. U.S. Patent 1,680,264.

(3) Lambuth, A.L., 1977. Soybean glues. In “Handbook of Adhesives,” I. Skeist ed. Van Nostrand Reinhold Co., New York, NY.

(4) Babcock, G.E., Smith, A.K., 1947. Extending phenolic resin plywood glues with proteinaceous materials. Ind. Engr. Chem. 39, 85-88.

(5) Kuo, M.L., Adams, D., Myers, D.J., Curry, D., Heemstra, H., Smith, J.L., Bian, Y., 1998. Properties of wood/agricultural fiberboard bonded with soybean-based adhesives. For. Prod. J. 48, 71-75.

(6) Zhong, Z.K., Sun, X.S., Wang, D.H., 2003. Wet strength and water resistance of modified soy protein adhesives and effects of drying treatment. J. Polym. Environ. 11, 137-144.

(7) Sun, X.S., Bian, K., 1999. Shear strength and water resistance of modified soy protein adhesives. J. Am. Oil Chem. Soc. 76, 977-980.

(8) Huang, W.N., Sun, X.S., 2000. Adhesive properties of soy proteins modified by sodium dodecyl sulfate and sodium dodecyl benzene sulfonate. *Ibid*. 77, 705-708.

(9) Zhong, Z.K., Sun, X.S., Fang X.H., Ratto, J.A., 2002. Adhesive strength of guanidine hydrochloride – modified soy protein for fiberboard application. Int. J. Adhes. Adhes 22, 267-272.

(10) Zhong, Z., Sun, X.S., 2001. Properties of soy protein isolate/polycaprolactone blends compatalized by methylene diphenyl diisocyanate. Polymer 42, 6961-6969.

(11) Cheng, E.Z., Sun X.S., 2004. Adhesive properties of modified soybean flour in wheat straw particleboard. Compos. Part A-Appl S. 35, 297-302.

(12) Steele, P.H., Kreibich R.E., Steynberg, P.J., Hemingway, R.W., 1998. Finger jointing green southern yellow pine with a soy based adhesives. Adhes. Age. 41, 49–56.

(13) Hojilla-Evangelista, M.P., Dunn Jr, L.B., 2001. Foaming properties of soybean protein-based plywood adhesives. J. Am. Oil Chem. Soc. 78, 567-572.

(14) Pizzi, A., 2006. Recent developments in eco-efficient biobased adhesives for wood bonding: Opportunities and issues. J. Adhes. Sci. Technol. 20, 829-846.

(15) Li, K., Peshkova, S., Geng, X., 2004. Investigation of soy protein-Kymene® adhesive systems for wood composites. J. Am. Oil Chem. Soc. 81, 487-491.

(16) Zhong, Z., Sun, X.S., Wang, D., 2007. Isoelectric pH of polyamide-epichlorohydrin modified soy protein improved water resistance and adhesion properties. J. Appl. Polym. Sci. 103, 2261-2270.

(17) Liu, Y., Li, K., 2002. Chemical modification of soy protein for wood adhesives. Macromol. Rapid Comm. 23, 739-742.

(18) Liu, Y., Li, K., 2007. Development and characterization of adhesives from soy protein for bonding wood. Intl. J. Adhes. Adhes. 27, 59-67.

(19) Nass, D.R., Kielbania, A.J., Lee, S.P., 2000. Thermosetting binder prepared with (hydroxyalkyl)urea crosslinking agent for abrasive articles. U.S. Patent 6,051,646.

(20) Ohlan, R., Balasubramanian, N., Ohlan, S., Narang, R., Judge, V., 2008. Synthesis and antimicrobian evaluation of urea inclusion complexes. Org. Comm. 1, 24-32.

(21) Deak, N.A., Johnson, L.A., 2006. Effects of extraction temperature and preservation method on functionality of soy protein. J. Am. Oil Chem. Soc. 84, 259-268.

(22) Nielsen, P.M., Petersen, D, Dambmann, C., 2001. Improved method for determining food protein degree of hydrolysis. J. Food Sci. 66, 642-646.

(23) American Society of Testing and Materials, 1999. Standard test method for evaluating properties of wood-base fiber and particle panel materials. Designation: D1037-99. West Conshohocken, PA, pp. 142-171.

(24) Espy, H.H., Rave, T.W., 1988. The mechanism of wet strength development by alkaline-curing polymer-epichlorohydrin resins. TAPPI J. 71, 133-137.

(25) Espy, H.H., 1995. The mechanism of wet-strength development in paper: A review. *Ibid.* 78, 90-99.

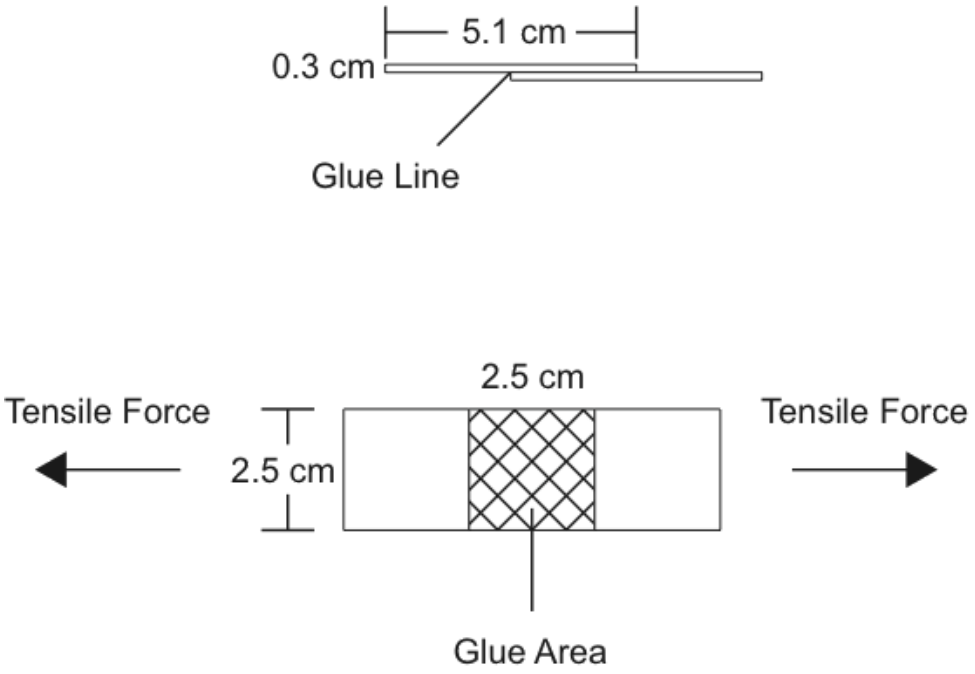

Figure 5-1. Lap shear dimensional diagram

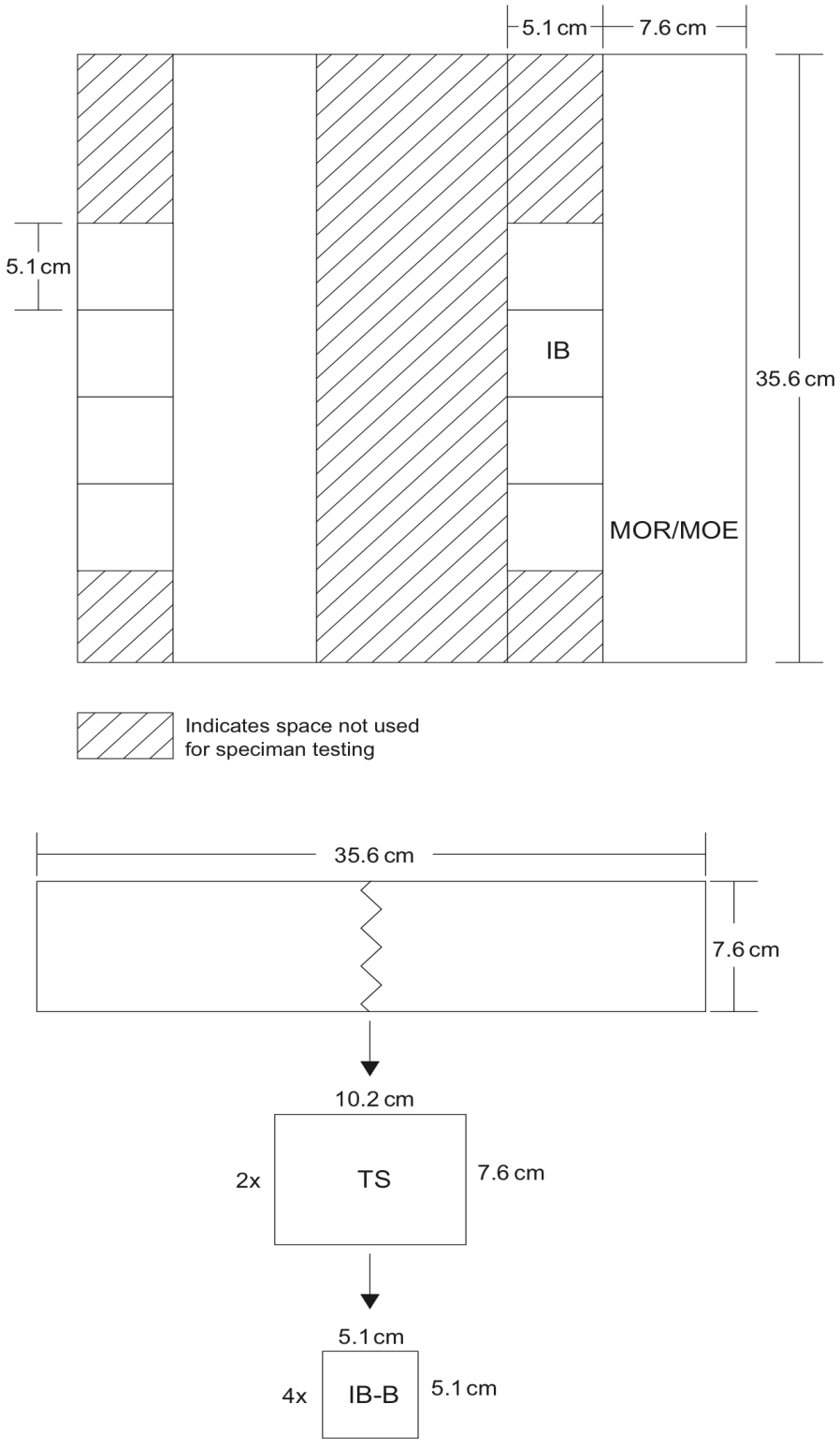

Figure 5-2. MDF testing specimen diagram

Table 5-1. Dry and wet shear strength of soy hydrolysate/PAE resin blends

Resin Formulation	Shear Strength (MPa)							
	Dry [1]		WSAD [2]		BWT [3] - D		BWT - W	
SPI	1.28	a	DL		DL		DL	
SPI-Urea	1.48	a	0.93	a	DL		DL	
SPI/PAE	3.28	c	3.21	b	3.01	a	2.45	a
SPI-Urea/PAE	3.33	c	3.38	b	3.11	a	2.68	a
SF	1.10	a	DL		DL		DL	
SF-Urea	1.25	a	DL		DL		DL	
SF/PAE	2.99	c	2.93	b	2.66	b	1.98	b
SF-Urea/PAE	3.25	c	3.18	b	2.93	a	2.47	a
PAE/Urea	2.48	b	2.43	c	1.92	c	1.37	c

[1] Dry strength is measure of shear strength (MPa) of cured lap shear specimens

[2] WSAD is measure of shear strength (MPa) following specimens soaking 20 h in 23°C distilled water

[3] BWT is shear strength (MPa) following two cycles of 4 h boiling water, measured

[4] Means in columns with common letters were not significantly different at the 5% level

Table 5-2. MDF mechanical properties for soy resin blends

Resin Formulation	Mechanical Properties					
	MOE (x1000 MPa)		MOR (MPa)		IB (MPa)	
SPI-Urea	2.44	a	21.4	a	0.59	a
SPI/PAE	2.76	a	28.5	b	1.05	b
SPI/Urea/PAE	2.59	a	27.9	b	1.01	b
SF-Urea	2.40	a	21.7	a	0.45	a
SF/PAE	2.90	a	27.3	b	0.87	c
SF/Urea/PAE	2.74	a	25.2	b	1.06	b
ANSI Standard, MDF[2]	2.40		24.0		0.60	

[1] Means in columns with common letters were not significantly different at the 5% level.

[2]American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

Table 5-3. MDF durability and wet strength internal bond characteristics

Resin Formulation	Dimensional Stability Characteristics					
	TS-2B (% swell)		TS-24S (% swell)		IB-B[3] (MPa)	
SPI-Urea	15.4	a	13.6	a	0.37	a
SPI/PAE	10.2	b	8.7	b	0.56	b,c
SPI/Urea/PAE	9.2	b	8.4	b	0.63	b
SF-Urea	16.2	c	14.3	a	0.35	a
SF/PAE	12.8	c	10.3	c	0.48	c
SF/Urea/PAE	9.1	c	8.9	b	0.61	b
ANSI Standard, MDF[2]	- - -		10.0		- - -	

[1] TS-2B is measure of percent thickness swell after specimen boiled in distilled water for 2 hours

[2] TS-24S is measure of percent thickness swell after MDF specimen soaked in distilled water at 23°C for 24 hours

[3] IB-B is internal bond strength after the TS-2B

[4] Means in columns with common letters were not significantly different at the 5% level within the type of soy component.

[5] American National Standard Institute (ANSI); MDF interior grade applications. ANSI A208.2-2002.

CHAPTER 6

Summary

Protein-based wood adhesives have been researched and in commercial use for nearly a century. Research over the past two decades has made great strides in identifying the potential for soy protein isolate and soy flour to be used for wood adhesives in today's marketplace. Chemical modifications are pivotal for protein adhesives to achieve adequate performance in the wide array of manufactured wood and composite products, but stand alone soy adhesives cannot match current adhesive standards.

Where this work stands apart from peer research is in developing modification techniques and performing applications testing. Chemically denatured soy protein isolate or soy flour can exhibit comparable strength to synthetic, petroleum based adhesives, but testing only lap shear strength ignores several essential variables – the most prominent being viscosity and the ability to be used in multiple application systems. Enzyme hydrolysis modifies soy flour more extensively than chemical modifications, is more controlled than alkaline hydrolysis, and significantly decreases viscosity, making the soy protein hydrolysates suitable for multiple applications.

When blended with phenol formaldehyde (PF), hydrolyzed soy flour produced no significant changes to internal bond, MOR, or MOE with as much as

20% soy solids. The degree of protein hydrolysis was an important factor, but up to 18% degree of hydrolysis did not diminish properties.

With the growing pressures of “green” chemistry, worker and consumer safety, and petroleum independence, new and unique adhesive formulations have significant academic and industry appeal. The degree of soy protein hydrolysis was also examined to achieve formaldehyde free adhesives. Polyamide-epichlorohydrin (PAE) is relatively new to wood adhesives, but the chemistry is well established and it has a long-standing tradition in the paper industry for enhancing wet strength. Soy/PAE resin blends exhibited high shear strength, mechanical strength, and water durability with as much as 90% soy solids. Less hydrolysis (<10% DH) is desirable to maintain strength in PAE resins compared to 18% for PF blends. Wet strength is a common concern when adhesives are formulated with soy flour. Wet strength diminishes significantly in both PF and PAE systems when working with soy flour hydrolysates compared to soy protein isolate.

Finally, adding urea to soy hydrolysates had a number of positive effects. It prevented the visible growth of mold and bacteria and helped stabilize the viscosity of hydrolysates. Soy flour blended with urea and then PAE maintained consistent viscosity over extended periods with no significant change in bond strength. Most important though, is that soy flour mixed with urea prior to PAE blending led to significant improvements in wet strength and water durability. Soy flour hydrolysates with urea had comparable traits to hydrolyzed soy protein isolate.

Looking ahead, there are numerous possibilities for soy based wood adhesives. Chemical denaturation has limited uses due to high viscosity of soy

protein isolate or flour dispersions. Hydrolysis leads to more possibilities by exposing more of the peptide side chains and increasing the amount of amine groups, but an additional crosslinker is almost assuredly required to create finished products that meet current industry standards. Traditional adhesives, such as PF, are compatible, but new and novel crosslinkers are more likely to emerge for future industry use.

ACKNOWLEDGEMENTS

I would like to thank my major professors for the opportunity to do my graduate studies at Iowa State University. It has been a great experience, and one where I have truly learned as much about myself as anything else.

Through my campus activities and leadership roles in the Graduate & Professional Student Senate I have had three exceptional contacts in the Division of Student Affairs. Vice President Tom Hill, Assistant VP Todd Holcomb, and Dean of Students Dionne Somerville, I appreciate more than I ever indicated that before or after most meetings, each of you checked in to see how everything was going. Probably more than anyone else, you three know how everything progressed and the struggles I came across. The opportunities I had in my roles with each of you was spectacular as well. Regardless of anything else, Dione, we both know that I represented the entire female voice on campus very well through design of new locker room at the west side recreation complex.

My parents have continued to be a solid foundation and sounding board for me. I congratulate the two of you on now having your third child finish their advanced degrees. We all look up to you for the advice, support, and friendship that you have offered us as we have grown into our adult lives and branched out on our own.

Last but not least, I want to thank my wife Becky for her support. At times it seems like we could not possibly be anymore different from one another, including the confusion and contempt in your voice when you say the word ‘science’, but your

creative and artistic approach to life has been a great diversion through all this. We met shortly after I assumed leadership responsibilities within the Graduate & Professional Student Senate and shortly before I found out Deland was leaving ISU. It is an understatement to say that I've been busy throughout our relationship, and you have dealt with that extremely well. It could not be any more fitting to use the last sentence of my dissertation than to say that I look forward to the future and having more time to spend with you.